

TITLE: "TO CARRY OUT RESEARCH ON IN-SITU RECOVERY OF
LLOYDMINSTER HEAVY OILS BY CAUSTIC FLOODING"

FINAL REPORT

by

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EXECUTIVE SUMMARY

The Lloydminster area of western Saskatchewan and eastern Alberta contains a huge reserve of moderately viscous to very viscous heavy crude oil. Thermal enhanced oil recovery processes are applicable in about 50% of these fields. For the other 50% of the deposits, chemical-based processes are required in order to maximise oil recovery efficiency. For chemical processes to be economically viable, the candidate chemicals have to be readily available, inexpensive and at the same time very effective. In this work, we have examined a number of chemical enhanced oil recovery options for a typical Lloydminster heavy oil reservoir. Waterflooding at 65°C yielded 12% more oil than was obtained at 25°C. This was largely due to the drastic drop in crude oil viscosity with a modest rise in temperature. Dilute aqueous solutions of sodium hydroxide, sodium metasilicate and sodium orthosilicate produced low interfacial tensions against the experimental crude oil. These tensions were influenced by the alkaline concentration, temperature and the contact time between the oleic and aqueous phases. The most surface active alkali was sodium hydroxide at the optimum concentration of 12.5 mM. The optimum concentration for the silicates was dependent on the operating temperature. For sodium metasilicate, its optimum concentration at 35°C and below was 2.5 mM. At higher temperatures, the optimum was 12.5 mM. The optimum concentration for sodium orthosilicate was 1.25 mM at 25°C and 2.50 mM at higher temperatures. Displacement tests conducted with these alkaline solutions in a tertiary injection mode gave additional recoveries (above those of the waterflood) of 10 to 50% depending on concentration and temperature. Oil recovery was highest at lower temperatures and at the optimum alkaline concentration. The high oil recovery values which were obtained at lower temperatures were consistent with the previously established dynamic interfacial tension trends. We found that the addition of small amounts of conventional surfactants to the alkaline solution lowered the interfacial tension even further at all operating temperatures. However, displacement tests conducted with these surfactant-enhanced alkaline solutions did not yield any additional oil over the values obtained with the caustic solutions alone. The reason for the poor performance of the surfactant-alkali formulations could be due to a chromatographic separation of the surfactant precursors (formed by the reaction between the alkali and acidic species present in the oil) from the active sulfonates of the conventional surfactants.

Proper mobility control is necessary in any chemical enhanced oil recovery process. The more viscous the oil is, the more important it becomes for the displacing fluid to have appropriate mobil-

ity. We have investigated the applicability of various polymers as thickening agents for both water and alkaline water fluids. Two polymers namely polyethylene oxide (molecular weight 4 million), and nonionic polyacrylamide (molecular weight 5 million) were the most effective ones within the range of temperatures and concentrations that we employed. Polyethylene oxide at a concentration of 0.5% by weight maintained a viscosity close to 140 mPa.s at 25°C and 6 rpm for more than 50 days. This polymer solution recovered 58% of the residual oil after waterflooding at 25°C and 71% at higher temperatures. Upon introduction of the polymer at the 0.5% concentration level to a mixture of NaOH and surfactant B-100, the viscosity of the mixture was within 90% of the value measured for the polymer alone. About 10 to 30% additional oil was produced with the formulations containing polyox, NaOH and B-100 compared to the recovery realised by using polymer solutions alone. The polymer-augmented alkaline solutions were most effective at lower temperatures and near the optimum NaOH concentration. Nonionic polyacrylamide at 0.5% concentration had a viscosity of about 40 mPa.s at 25°C. In the presence of NaOH and B-100, the polymer increased the viscosity of the mixture to 1300 mPa.s at 25°C (measured for the solution containing 25.0 mM NaOH). Alkali-surfactant-polymer solutions containing nonionic polyacrylamide manifested an increase in viscosity with age over a period of 70 days. The oil recovery figures obtained with these polymer-enhanced alkaline solutions were comparable to those obtained with the polyox-based formulations.

We have proposed an equilibrium interfacial tension model to account for the interaction of NaOH solutions with the experimental oil at the various operating temperatures. This model quantified the key parameters that influence equilibrium interfacial tensions. We found that the ionization constant of acids present in the crude oil was strongly influenced by temperature. An Arrhenius-type correlation was found to be satisfactory in representing this temperature effect. By using this model, we were able to predict the prevailing equilibrium interfacial tension under flow conditions. Finally, we have shown how fractional flow analysis can be used in conjunction with this equilibrium interfacial tension model to predict fractional flow rates of oil and water for the case of the base caustic flood.

SOMMAIRE EXECUTIF

La région de Lloydminster, située au Saskatchewan de l'ouest et en Alberta de l'est, contient de vastes réserves du pétrole brut moyennement ou très visqueux. Des méthodes thermiques de récupération assistée du pétrole peuvent être appliquées dans quelques 50% de ces puits. Quant aux 50% qui restent, des procédés de lavage basés sur l'application de produits chimiques sont nécessaires. Pour réussir sur la base économique, un produit chimique proposé doit être facilement disponible, peu dispendieux et, en même temps, très efficace. Dans le cadre de ce projet, nous avons examiné quelques options en ce qui concerne l'application de la récupération assistée aidée par des produits chimiques dans le cas d'un puits typique de Lloydminster de l'huile lourde. Lavage par l'eau à 65°C a produit 12% plus de l'huile qu'à 25°C. On peut expliquer cela par la chute dramatique de viscosité de l'huile due à l'augmentation modeste de la température. Les solutions diluées de l'hydroxyde de sodium, du metasilicate de sodium et de l'orthosilicate de sodium dans de l'eau produisaient des tensions interfaciales très faibles vis-à-vis le pétrole brut. Les valeurs de la tension étaient influencées par la concentration de l'alcali, par la température et par le durée de contact entre la phase aqueuse et oleïque. L'agent alcalin le plus actif était l'hydroxyde de sodium à la concentration optimale de 12.5 mM. La concentration optimale des silicates dépendait sur la température. Dans le cas du metasilicate de sodium, la concentration optimale était 2.5 mM à 35°C et dessous mais 12.5 mM à des températures plus élevées. La concentration optimale de l'orthosilicate de sodium était 1.25 mM à 25°C mais cette valeur était 2.5 mM à plus hautes températures. Les expériences de déplacement (lavage) faits avec les solutions alcalines mentionnés ci-haut de manière tertiaire ont démontré des recouvrements additionels du pétrole (au-dessus de ceux obtenu dans le cas du lavage par l'eau) de 10 à 50% suivant la température. Le recouvrement du pétrole était le plus haut à des faibles températures et à la concentration optimale de l'alcali. Les valeurs très élevées de recouvrement obtenues à faibles températures étaient consistantes avec les tendances déjà observées de la tension interfaciale dynamique. Nous avons aussi trouvé que l'addition de petites quantités de surfacteurs conventionnels à la solution alcaline a supprimée encore plus la tension interfaciale à toutes les températures opérationnelles. Cependant les expériences de lavage avec ces solutions alcalines dotées des surfacteurs n'ont apporté aucune augmentation de la récupération du pétrole par rapport à celle observée dans le cas de la solution

alcaline toute seule. Il semble que la mauvaise performance des formulations surfacteur-alcali pourrait être causée par de la séparation chromatographique entre des précurseurs des agents tensio-actifs formés par la réaction chimique entre l'alcali et l'acide présent dans l'huile, et les sulfonates actifs trouvés dans les surfacteurs conventionnels.

Le contrôle de la mobilité est une condition préalable pour tout procédé chimique de la récupération assistée du pétrole. Le plus le pétrole est visqueux, le plus important cela devient pour le fluide déplaçant d'avoir une mobilité appropriée. Nous avons étudié la possibilité d'utiliser de différents polymères comme épaississeurs dans le cas de l'eau et des fluides alcalines. Deux polymères, à savoir polyéthylène oxyde (masse moléculaire 4 million) et polyacrylamide non-ionique (masse moléculaire 5 million) ont été les plus efficaces dans la gamme des températures et des concentrations utilisées. Polyéthylène oxyde a la concentration de 0.5% par masse retenait la viscosité proche à 140 mPa.s à 25°C et 6 rpm pendant plus que 50 jours. Cette solution polymérique a recouvert 58% de l'huile résiduaire après le lavage par l'eau à 25°C, et 71% à plus hautes températures. Lorsque ce polymère a été ajouté, à la même concentration de 0.5%, à un mélange de NaOH et le surfacteur B-100, la viscosité de la solution a demeuré en dedans de 90% de la valeur mesurée avec le polymère tout seul. A peu près 10 à 30% de l'huile additionnelle a été récupéré en utilisant les formulations contenant du polyox, NaOH et B-100 par rapport à la récupération réalisée en utilisant seules les solutions polymériques. Les solutions alcalines additionnées de polymères étaient les plus efficaces à des faibles températures et dans la proximité de la concentration optimale de NaOH. Le polyacrylamide non-ionique ayant la concentration de 0.5% a eu la viscosité d'approximativement 40 mPa.s à 25°C. En présence de NaOH et B-100, ce polymère a augmenté la viscosité du mélange à 1300 mPa.s (comme mesuré pour une solution 25.0 mM NaOH). Les formulations alcali-surfacteur-polymère contenant du polyacrylamide non-ionique ont manifesté une augmentation de leur viscosité avec l'âge sur une période de 70 jours. Les résultats de récupération obtenus avec ces formulations alcalines additionnées du polyacrylamide étaient comparables à ceux obtenus avec des formulations basées sur le polyox.

Nous avons proposé un modèle de la tension interfaciale d'équilibre afin de décrire l'interaction des solutions de NaOH avec le pétrole aux conditions différentes de température. Ce modèle évalue les paramètres d'importance qui affectent les tensions interfaciales d'équilibre. Nous avons trouvé que les constantes d'ionisation des acides présents dans le pétrole brut sont fortement influencées par la température. Une

correlation d'après Arrhenius a satisfait au besoin d'exprimer l'effet de la température mentionné ci-haut. En utilisant ce modèle, il a été possible de prédire la tension interfaciale d'équilibre dans l'état d'écoulement. Finalement, nous avons démontré comment l'analyse d'écoulement fractionnaire peut s'appliquer, conjointement avec le modèle de la tension interfaciale d'équilibre, au but de la prédiction du débit fractionnaire de l'huile et de l'eau dans le cas du lavage alcalin de base.

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1 INTRODUCTION

The Lloydminster area of West-Central Saskatchewan and East-Central Alberta contains an estimated heavy oil reserve of about 11 billion m³. According to Selby et al.[1], the viscosity of the crude at reservoir conditions varies from 500 to 4000 mPa.s. Traditionally these reservoirs are subjected to secondary waterflooding in order to improve primary recovery. The combination of primary production and secondary waterflooding results in about 8 to 10% recovery of the original oil in place.

Conventional waterflooding at reservoir conditions cannot recover any significant additional oil due to the unfavourable mobility of the drive fluid which in turn leads to fingering and channeling. A concerted research and development effort is needed in order to exploit these huge heavy oil deposits efficiently. The various options that can be utilized are collectively referred to as Enhanced Oil Recovery (EOR) processes[2]. Thermal processes, notably steam flooding and steam stimulation are the most commonly used EOR techniques for the recovery of heavy crudes. In steam flooding and steam stimulation, sensible and latent heat is transported to the reservoir and subsequently transferred to the relatively cold crude. As the oil heats up, its viscosity drops and the resulting hot waterflood is able to sweep the reservoir better. In this way, more oil can be produced. However, if the transfer of heat from the steam to the oil is inefficient, little or no additional oil will be produced. Selby et al.[1] believe that in about 50% of the heavy oil deposits, efficient heat transfer cannot be guaranteed. Thus, a non-thermal process would be preferred. For these reservoirs, the oil occurs in multiple zones of relatively thin sands, or the formation exists at large depths and has low permeabilities. In some cases, the oil zone is underlain by a large aquifer. Under these circumstances, the incident heat is quickly dissipated to adjoining rocks and aquifers.

Some non-thermal applications are designed to lower the viscosity of the crude oil just like a thermal process. Super-critical fluids such as carbon dioxide are injected under pressure. As the gas dissolves in the crude oil, swelling occurs and the viscosity of the crude decreases. The drive water which usually follows the CO₂ slug is then able to sweep the reservoir better and thus more oil is recovered. The conditions under which these high pressure fluids are injected do not permit complete miscibility with the oil. The result is that a significant amount of the oil remains trapped in the fine pores of the reservoir sands by capillarity. In order to mobilize such trapped oil, the injection of surface active agents becomes necessary. Surfactants added to the flood water adsorb

at the oil-water interface thereby lowering the interfacial tension (IFT). When the IFT is reduced to very low values, the stranded oil is mobilized and subsequently produced. Direct introduction of surfactants in the drive fluid gives rise to surfactant or micellar flooding[3,4]. Surfactant flooding is best suited to light crudes (with viscosities below 40 mPa.s) in low salinity reservoirs. The favoured reagent in the case of heavy crudes is an alkali.

The ability of alkaline solutions to recover additional oil from subterranean reservoirs has been recognized since the time of Atkinson[5]. More recent publications[6-9] have confirmed the effectiveness of alkalis for the recovery of acidic crudes. Dranchuk et al.[6] obtained 100% recovery improvement at breakthrough by displacing a Lloydminster crude with 0.1% (by weight) NaOH solution. Scott et al.[7] reported improved recoveries (over waterflood) of 4 and 31% when a 1200 mPa.s Lloydminster crude was displaced with 0.01 and 0.05% NaOH respectively. Farouq Ali[8] reported that by the continuous injection of a caustic solution, an improved oil recovery of about 60% above the waterflood result could be achieved. Alkalis are not only effective against heavy oils, they are relatively abundant and cheap. It is now generally believed that alkaline reagents added to the flood water react with carboxylic acids native to the crude oil. These acid/base-like reactions lead to the generation of surface-active soaps which adsorb at the oil-water interface. As the in-situ surfactants accumulate at the interface, the IFT is gradually reduced to very low values. Under such circumstances, residual oil will be mobilized resulting in an improved oil recovery efficiency.

The precise mechanisms of crude-alkali interactions are still unclear. Some of the mechanisms that were recently proposed include wettability reversal[10-12], emulsification with entrapment or entrainment[13], partial wettability reversal and emulsification with coalescence[14]. No one single mechanism can satisfactorily account for the behaviour of crude/alkali systems under all operating conditions of salinity, alkaline concentration and temperature. The general consensus appears to be that for a given caustic system to be effective against a target crude, the IFT would have to be lowered to very low values such as would promote the formation of emulsions. The stability of the emulsion would be such as to allow the entrained oil droplets to coalesce into a stable oil bank. The fact that no one mechanism has been able to explain satisfactorily the interaction of different alkalis with various crudes, demonstrates that our understanding of the underlying physico-chemical phenomena is not yet complete. Alkaline formulations which perform very well in laboratory tests do not always produce significant amounts of additional oil in actual field trials. Of the 15 alkaline floods conducted in Canada and the United States between 1970 and 1985, Selby

et al.[1] reported that only one test proved successful. The majority of the tests were abandoned due to poor performance.

An injected alkaline solution is subject to three coupled interactions[9,14,15] namely, alkali-crude, alkali-connate water and alkali-matrix minerals. Laboratory experiments can only simulate alkali-crude interactions in a rather limited manner. The key to the development of efficient alkaline formulations lies in obtaining a thorough understanding of these three interactions. In this work, we hope to elucidate some of the important variables that influence crude/alkali interactions.

The type of alkali selected for a given application is one important variable that influences oil recovery. The most commonly used alkalis are sodium carbonate, sodium hydroxide and sodium silicates. Campbell[16,17] opined that only sodium hydroxide and sodium orthosilicate have sufficient alkalinity to react quickly with crude oil acids. Against both Huntington Beach and Wilmington crudes, he found that sodium orthosilicate was more effective than sodium hydroxide when both were used at the same concentrations. Novosad and McCaffery[18] reported that both alkalis gave comparable oil recoveries when they were used to displace Wainwright crude. Some reseachers[19,20] found sodium carbonate to be quite effective particularly when polymers and surfactants were also incorporated. Thus, the logical starting point in the design of an alkaline flood is the development of a suitable screening strategy for the selection of the most suitable alkali. Such a strategy has been developed in this study.

Another important variable in the study of crude/alkali interactions is the dependence of the IFT on alkaline concentration, reservoir salinity and contact time between the oleic and aqueous phases. Depending on the prevailing alkaline concentration, the initial IFT may fall by two or more orders of magnitude to a minimum value within 10 to 20 minutes of phase contact. After the attainment of this minimum, the IFT could rise rather dramatically to much higher values. This so called dynamic IFT phenomenon has been recognized by several workers[21-23]. Ideally, one would like to see the IFT drop to ultra-low values at early contact times and to be kept low even at extended contact times. In this work, we have investigated various means of achieving this desirable IFT trend.

The third variable worthy of consideration is temperature. Most Canadian heavy oil deposits are considered to be cold (reservoir temperatures below 30°C). At such reservoir temperatures, the average viscosity of a moderately viscous heavy crude is about 1000 mPa.s. However, the viscosity usually falls off rapidly with a relatively small rise in temperature. Consequently, hot water flooding

would be able to effect a considerable improvement in oil mobility which in turn would lead to a significant additional oil recovery. Thus, conducting an alkaline flood at elevated temperatures is potentially beneficial. Babu et al.[24] investigated the dynamic IFT behaviour of NaOH solutions (with and without NaCl) against Lloydminster and Cold Lake crudes at temperatures of 35, 45 and 55°C. While temperature had little or no effect on the dynamic IFT of the Cold Lake/caustic system, the Lloydminster/caustic system produced dynamic IFT minima which decreased as temperature was increased. After the attainment of the minimum, the IFT tended to rise much faster to even higher values at longer contact times and higher temperatures. The effect was more pronounced in the presence of NaCl. Mehdizadeh and Handy[25] studied the dynamic IFT behaviour of NaOH, Na_2SiO_3 and Na_2CO_3 against Wilmington crude at temperatures ranging from 60 to 180°C. They reported that the IFT increased in all cases with an increase in temperature, the increase in tension being more pronounced for the NaOH system than for the other alkalis. In displacement tests which they conducted at the same elevated temperature conditions, the authors found that oil recovery at lower temperatures was comparable to those obtained at higher temperatures. Cooper[26] also carried out alkaline displacement runs at temperatures of 54, 71 and 88°C. He reported incremental oil recoveries at all temperatures based on the recovery values for distilled water at similar temperatures. The NaOH solution was most effective at 71°C. These temperature-related studies suggest that we should be looking at alkaline waterflooding at moderate temperatures rather than using steam impregnated with alkali.

In a recent review, Surkalo[27] described the micellar/polymer process as a technical success but an economic failure. The economic failure was directly linked to the high cost of surfactants. He suggested that the economics of the process could be improved by substituting the costly surfactants with less expensive materials such as alkalis. The author showed that the addition of a small amount of petroleum sulfonate to an alkaline solution resulted in a reduction in IFT by two orders of magnitude. Reisberg and Doscher[28] had reported significant additional oil recovery when an anionic surfactant was added to the caustic solution. Thus, surfactant-enhanced alkaline (SA) processes have emerged as a practical way of improving the performance of an alkaline flood. The best way to optimise the SA process is still a subject of continuing research. Nelson et al.[29] favour the use of activity maps with emphasis on phase compatibility, others such as Taylor et al.[20] prefer dynamic IFT measurement. While recognising the importance of these two approaches, we have in this work, expanded the optimization criteria of the SA system by incorporating a screening

strategy to select the most suitable surfactant, and we have also elected to use a wide range of temperatures for the entire study. A new element which we have introduced in an effort to improve both the efficacy and economics of the alkaline flood is the addition of a cosurfactant in what will then become a cosurfactant-surfactant alkaline (CSSA) process. Based on the impressive results from our earlier work[30,31], we elected to use lignosulfonates as possible cosurfactants in the SA systems.

If a given alkaline formulation is to achieve its ultimate oil recovery potential, then improvement in the interfacial efficacy as well as in viscosity has to be realized. The former is achieved by the SA or CSSA process while the latter is handled by the alkaline-polymer(AP) process. While the addition of a polymer to the alkaline solution is intended to improve its viscosity, it is not uncommon to effect some improvement in interfacial activity as well. Such an improvement was reported by Huang et al.[19]. The first task in the design of an AP system is the selection of the working polymer. Needham and Doe[32] found polyacrylamides and biopolymers to be the most commonly used polymers in enhanced oil recovery practice. The merits and demerits of these two classes of polymers were also discussed by the authors. Polyacrylamides can be cationic, anionic or nonionic in nature. Both polyacrylamide and biopolymer products are available in a wide range of molecular weights and molecular weight distributions. The task of selecting a suitable polymer formulation is therefore a formidable one. We have not only expanded the base for selecting a suitable polymer for the alkaline formulation, but in addition, we have conducted a detailed rheological study of the polymer-caustic system in a manner that has not been reported before.

An AP system may be designed to alter the permeability of the reservoir to a more favourable level. Such was the aim of an AP system which was developed by Alam and Tiab[33]. In this scheme, a polymer slug was injected ahead of the alkaline solution and it resulted in an improved oil recovery. In order to combine the benefits of the SA and AP processes, Shuler et al.[34] proposed the so-called micellar/alkali/polymer (MAP) flood. In this scheme, a small micellar/polymer (MP) slug was injected ahead of a larger AP slug. The authors reported that the MAP system recovered about 80% of waterflood residual oil. The most convenient way is to combine the alkali, the surfactant (with or without cosurfactant) and the polymer all in one compatible formulation. Such a formulation was alluded to by Surkalo[27] and was actually used by Lin et al.[35] who reported an incremental oil recovery (over the waterflooding result) of 47% of the original oil in place.

Our objective in this study was therefore to develop an optimized MAP formulation for the

target crude. This optimization was carried out by a carefully planned screening strategy using interfacial and physical property measurements at several temperatures and reagent concentrations. Each promising formulation was then further evaluated for its oil recovery potential by linear displacement tests in artificial sandpacks. Finally, we have attempted to calculate pertinent physico-chemical parameters that influence the behaviour of these systems.

2 EXPERIMENTAL

2.1 Specification of Materials

Three alkalis were used in this study, namely sodium hydroxide, sodium metasilicate and sodium orthosilicate. The highest purity grade commercially available was used for the preparation of the working solutions. In the case of sodium orthosilicate, a 500 mM stock solution was prepared by mixing stoichiometric amounts of NaOH and Na_2SiO_3 . The detailed specifications as well as the suppliers of the various reagents have been listed in Table 1. Three conventional surfactants namely Petrostep B-100, Petrostep B-110 and Petronate L were also used in the study. All surfactants are synthetic alkylaryl sodium sulfonates with varying molecular weights, active sulfonate and free oil concentrations. Five polymeric materials were also used in the study. They include a polysaccharide, two non-ionic polymers, one cationic polyacrylamide and one anionic polyacrylamide. Except where otherwise stated, each reagent was used as supplied. Water used for the preparation of the working solutions was singly distilled and then passed through a four module cartridge purification unit. This water purifier consisted of a particulate removal cartridge in series with an organic carbon removal system, followed by a cation and then an anion separation cartridge. Before making up the solutions, the water was again boiled, cooled in an air tight container and finally deaerated under vacuum.

The crude oil used in the study was Saskoil Canadian Reserve Court crude which was supplied by Saskoil from well number 4-25-33-28 W3M. Properties of this crude are listed in Table 2.

2.2 Dynamic IFT Measurement

Two different measurement systems were used for the dynamic IFT studies. Tensions above 20 mN/m were measured with the aid of the Fisher du Nouy ring tensiometer using essentially the procedure which was outlined previously[36]. For precise tension measurement at temperatures above ambient conditions, thermostating of both the oleic and aqueous phases was necessary. This was achieved by using water baths equipped with good temperature control. While the samples were being thermostatted, the jacketed vessel which normally held the experimental fluid samples in the tensiometer was also brought to the desired temperature by circulating water from another water bath. After a predetermined interface aging period, the platinum ring was then pulled through the interface and the resulting tension was recorded on the on-line analog meter

which had been previously calibrated. All measurements were carried out in duplicate.

For tensions below 20 mN/m, use was made of the in-house modified spinning drop tensiometer. A schematic diagram of the modified tensiometer is given as Fig. 1. The major modification carried out was the incorporation of a photographic unit in order that changes in the profile of the experimental oil droplet could be captured on photographic film. Measurements of the dimensions of the droplet as a function of spinning time could then be carried out from these photographs. In reacting systems such as crude oil/alkaline systems, tensions could change very rapidly. Consequently, the experimental oil droplet would elongate and contract at a rate that would make on-line measurements difficult and inaccurate. It is also desirable to achieve a good control of the temperature of the oleic and aqueous samples both before and during tension measurement. In order to achieve this end, we have modified the temperature control system of the classical tensiometer, as described elsewhere[37]. For measurements at ambient conditions, air was cooled by passing it through a coil of tubes immersed in a water bath, and the cool air was then passed over the rotor shaft and its housing. The University of Texas tensiometer is equipped with an internal heater for measurements at elevated temperatures. However this heater is activated only when the rotor is running. Once the rotor is turned off (for example during the loading of the capillary tube), the temperature in the measurement chamber drops off very rapidly. In order to avoid such thermal shocks, we developed a scheme in which air was heated by passing it through coils embedded in an oven and then circulated through the measurement chamber. As with the ring tensiometer measurements, we had to preequilibrate the oleic and aqueous samples before they were loaded into the capillary tube. The high speed camera enabled photographs of the oil droplet to be taken at any desired time intervals. At the end of the experiment, the film was processed into negatives, and from these negatives we were able to measure precisely the dimensions of the droplet at any desired interfacial age. These measurements were made with the aid of an optical comparator equipped with direct digital readouts. Depending on the ratio of the length to the width of the droplet, the tension was then calculated using Vonnegut's formula[38] or the alternative solution of Slattery and Chen[39].

2.3 Physical Property Measurements

The physical property data for all solutions were experimentally determined using standard equipment and following routine procedures. The pH of all aqueous solutions was measured with the aid

of a high pH glass electrode in conjunction with a standard calomel reference electrode. The pH meter was standardized in the usual manner using two different calibrating buffers. Measurements at temperatures above 45°C could not be carried out due to the fact that the pH of the buffers was unknown at such conditions. Density measurements were carried out with the Anton Paar Model DMA 48 density meter. This equipment gave direct readings of the density of the sample at any desired temperature based on the densities of air and distilled water as reference substances. Care was however taken to degas all samples before they were loaded into the density meter.

The viscosity of all aqueous solutions (excluding those that contained polymers) was determined with the aid of calibrated Cannon-Fenske viscometers. In the case of the crude oil, a reverse flow viscometer had to be used due to its opaque nature. For any given solution, the viscosity was measured three times and the average time taken for the meniscus to travel between the viscometer marks was used to calculate the viscosity of the fluid. All solutions that contained polymers were non-Newtonian in nature. For such solutions, the Cannon-Fenske viscometer was inappropriate. The Brookfield Synchro-Lectric viscometer was used at speeds of 6, 12, 30 and 60 rpm. All such measurements were carried out using spindle number 1 for viscosities below 100 mPa.s at 60 rpm, and spindle numbers 2 and 3 for higher values. The age of the polymer and caustic-polymer solutions was found to influence the viscosity. Accordingly, the viscosity measurements were carried out not only at different temperatures for each formulation, but also at different aging periods for the same system.

2.4 Procedure for Displacement Tests

The setup used for the displacement runs is depicted in Fig. 2. It consisted of vessels (or reservoirs) for holding and heating the aqueous solutions, a reservoir for the crude oil, a high pressure positive displacement pump for injecting the drive fluid, a low pressure positive displacement pump for injecting oil into the column, a stainless steel core holder packed with sand (which serves as the porous medium), an electrically heated wooden box in which the core holder was placed, and 1/4 inch tubing linking the vessels to the core holder and from the core holder to the effluent collection system. The effluent collection system consisted of an inverted buret mounted inside a larger cylindrical vessel. The external vessel was filled half way with a 5% salt solution. Initially, the buret was also filled to the mark with the same salt solution. The effluent passed directly into the buret where an oil layer or an emulsion layer collected. The total volume of oil or emulsion could

be determined directly from the buret while the effluent volume was obtained from the increase in the level of the liquid contained in the external vessel. The rest of the apparatus included a vacuum pump for deaerating the porous medium prior to oil saturation, and isolation/link up valves for controlling the flow of fluids into and out of the bed.

The characteristics of the porous medium used for all runs are given in Table 3. The core holder was packed dry to a constant porosity, and the porous bed was then put on vacuum for at least twelve hours. Thereafter, the bed was heated up slowly to the desired flood temperature. Once the desired temperature was attained, oil saturation commenced. In the meantime, the reservoirs containing the aqueous solutions were heated indirectly by circulating hot water from a bath through coils placed inside the vessels. The displacement runs were conducted in two modes, namely, a secondary mode in which distilled water was injected continuously for a total of three pore volumes, and a tertiary mode in which two pore volumes of the alkaline solution (or polymer solution) were injected following the injection of one pore volume of water. The injection rate was maintained relatively constant for all runs at 3.99 mL/min (2.7 m/day).

Whenever an emulsion was produced (which was the case in most of the caustic floods), the apparent volume of oil was obtained from the buret reading. Once the buret was full, the aqueous phase was removed and the oleic layer was emptied into centrifuge bottles. A small amount of 0.06 M hexadecyltrimethylammonium bromide solution in water was then added to each bottle before the emulsion was centrifuged in a laboratory centrifuge for about one hour. If the emulsion did not break up neatly, the sample was then distilled using the Dean and Stark distillation kit in accordance with ASTM D-95. Before commencing the distillation, the emulsion was diluted with several volumes of toluene. Once the exact oil content of the emulsion had been determined, the apparent reading taken from the buret was then corrected.

3 MATHEMATICAL MODELLING/NUMERICAL SIMULATION

3.1 General Principles of the Simulation

In this investigation, we have studied the dynamic interfacial tension behaviour of several alkaline formulations under essentially a batch, non-flow condition. Both spinning drop and ring tensiometries require working with batch systems. Under flow conditions such as in real caustic floods, the IFT prevailing at the leading edge of the caustic front is expected to differ substantially from that determined under non-flow conditions. This difference is associated with the continuous attenuation of the initial alkaline concentration due to dilution with connate water, reaction with matrix minerals, chromatographic separation of the constituents present in the original formulation and adsorption/retention losses. The first objective of these simulation studies was to develop a model for predicting equilibrium IFT in caustic/crude systems under flow conditions from tension data obtained under batch, non-flow conditions. We restricted our attention to the NaOH/crude oil system alone. The treatment can be extended to the sodium silicate/crude system as well as to alkaline formulations containing surfactants and polymers. Sodium silicates pose a peculiar problem due to the tendency of the monosilicate anion to hydrolyse in water to more complex species[16]. The degree of hydrolysis and the distribution of siliceous species depends on the pH of the solution, the total electrolyte concentration and the temperature. In order to develop a realistic model of the silicate/crude oil system, one should have a good understanding of these hydrolysis reactions.

In developing this equilibrium IFT model for the NaOH/crude oil system, we seek values of the important parameters that govern the interaction of the alkali with the crude oil at various temperatures and for the different NaOH concentrations. Having determined these parameter values, we then attempted to establish a definite functional relationship between the parameter and temperature in the form of a correlation. In the second part of the simulation study, we used the equilibrium IFT model to calculate relative permeability values for the oil and aqueous phases as a function of wetting phase saturation. Finally, we applied the predicted relative permeability values in the calculation of the fractional flow rates of water and oil as a function of wetting phase saturation. This information is necessary in order to predict the oil recovery potential of a given alkaline flood.

3.2 Equilibrium IFT Model

We assume that the acids present in the crude oil can be represented by a single hypothetical species labelled 'HA'. This assumption is in line with the treatment of Chan and Yen[40] as well as Ramakrishnan and Wasan[41]. Additionally, we neglect adsorption and dispersion effects. The IFT at any given caustic concentration and temperature is uniquely determined by the interplay of diffusive and sorption kinetic forces that prevail at the oil-water interface. The system chemistry is similar to that which was developed previously[42]. We now outline the essential features of the model as follows:

3.2.1 Interfacial Reactions and Equilibria Relationships

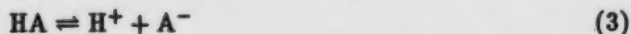
1. Partitioning of the acid, HA, to the aqueous sublayer ;

$$HA_o = HA_w \quad (1)$$

Reaction 1 is governed by the partition coefficient, K_p , which is given by ;

$$K_p = \frac{CHA_o}{CHA_w} \gg 1 \quad (2)$$

2. Dissociation of the acid at the aqueous side of the interface according to the reaction ;



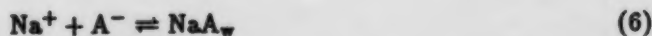
The ionization constant for reaction 3 is given by ;

$$K_{HA}^D = \frac{C_{H^+} C_{A^-}}{CHA_w} \quad (4)$$

The equilibrium ionic concentrations are influenced by the ionic product of water as follows ;

$$K_w = C_{H^+} C_{OH^-} \quad (5)$$

3. Formation of the surface inactive soap complex at the aqueous side of the interface in accordance with the reaction ;



and this too has an associated equilibrium constant defined by ;

$$K'_{NaA_w} = \frac{C_{Na^+} C_{A^-}}{C_{NaA_w}} \quad (7)$$

4. Partitioning of the soap complex to the oleic phase with the distribution ratio given as follows ;

$$K_D = \frac{C_{NaA_w}}{C_{NaA_o}} \ll 1 \quad (8)$$

By combining equations 7 and 8 , we can define a global equilibrium parameter for the desorption of A^- to the oleic phase, thus ;

$$\begin{aligned} K_s &= K'_{NaA_w} K_D \\ &= \frac{C_{Na^+} C_{A^-}}{C_{NaA_o}} \end{aligned} \quad (9)$$

3.2.2 Model Equations

We start by relating the anion concentration to the equilibrium parameters. The conservation equations for the surface active species are written as follows ;

- i Mass balance for A^- ;

$$V_w C_{HA_w} + V_w C_{A^-} + V_o C_{HA_o} + V_o C_{NaA_o} = V_o (C_{HA_o})_o \quad (10)$$

- ii Mass balance for Na^+ ;

$$V_w C_{Na^+} + V_o C_{NaA_o} = V_w (C_{OH})_o \quad (11)$$

- iii Charge balance in the aqueous phase ;

$$C_{Na^+} + C_{H^+} = C_{OH^-} + C_{A^-} \quad (12)$$

For the working aqueous phase pH , C_{H^+} is negligible and C_{A^-} is small compared to C_{OH^-} , so equation 12 simplifies to ;

$$C_{Na^+} = C_{OH^-} \quad (13)$$

By combining equations 9 and 11 , and using equation 13 , we obtain the following :

$$\begin{aligned} C_{Na^+} &= C_{OH^-} \\ &= \frac{(C_{OH^-})_o}{\left[1 + \frac{V_o}{V_w} \frac{C_{A^-}}{K_s}\right]} \end{aligned} \quad (14)$$

From equations 2 and 4 , we may write ;

$$\frac{K_p}{K_{HA}^D} = \frac{C_{HA_o}}{C_{H^+} C_{A^-}} \quad (15)$$

We now use equation 5 to eliminate C_{H^+} from equation 15 and the result is as follows ;

$$C_{HA_0} = \frac{K_w K_p C_{A^-}}{K_{HA}^D C_{OH^-}} \quad (16)$$

Finally we substitute for C_{NaA_0} using equation 9 , for C_{HA_0} using equation 4, and for C_{HA_0} using equation 16, all into equation 10 . The result is the following ;

$$C_{A^-} = \frac{(C_{HA_0})_0}{\left[\left(\frac{V_w}{V_0} \left(1 + \frac{K_w}{K_{HA}^D C_{OH^-}} \right) \right) + \frac{K_w K_p}{K_{HA}^D C_{OH^-}} + \frac{C_{OH^-}}{K_s} \right]} \quad (17)$$

3.2.3 Relating Anion Concentration to IFT

We adopt the analysis of Davies and Rideal[43] and write down the rates of adsorption and desorption of the active anion employing Langmuirian sorption kinetics. At equilibrium, these rates are equal. We can relate the bulk concentration of the active anion to the sub-layer concentration by means of the Poisson-Boltzmann relationship, thus;

$$C_{A^*} = C_{A^-} \exp\left(-\frac{z_A \psi_0 \epsilon N}{RT}\right) \quad (18)$$

We then use equation 18 to eliminate the sublayer concentration from the adsorption rate equation. The equilibrium bulk concentration of the active anion is then given by the following;

$$C_{A^-} = \frac{(B_2/B_1) \Gamma \exp\left(-\frac{W}{RT}\right)}{\left\{ \left(1 - \frac{\Gamma}{\Gamma_{max}} \right) \exp\left(-\frac{z_A \psi_0 \epsilon N}{RT}\right) \right\}} \quad (19)$$

1. The interfacial potential in terms of the Gouy-Chapman model is given as follows:

$$\psi_G = -\frac{2kT}{\epsilon} \sinh^{-1} \left\{ \frac{\sigma}{\sqrt{C_i}} \sqrt{\left[\frac{500\pi}{D_c RT} \right]} \right\} \quad (20)$$

At the working temperature of say 25° C, the values of the other physical constants, namely, k , R , ϵ , and D_c , are substituted into equation 20 and the result is as follows ;

$$\psi_G = -51.4 \sinh^{-1} \left(\frac{136.9}{A \sqrt{C_i}} \right) \quad (21)$$

2. We now seek to relate Γ to the equilibrium surface pressure.

This is accomplished via the Frumkin-Volmer-Davies-Hachisu (FVDH) equation of state[42] which is restated as follows:

$$\begin{aligned} \Pi &= \Pi_s + \Pi_r \\ &= \gamma_0 - \gamma \\ &= \frac{kT}{A_0} \ln \left(\frac{A}{A - A_0} \right) + \sqrt{\left(\frac{8D_c N C (kT)^3}{10^3 \epsilon^2} \right)} \left[\cosh \left(\frac{\epsilon \psi_0}{2kT} \right) - 1.0 \right] \end{aligned} \quad (22)$$

If Γ is expressed in moles per m^2 , then A is evaluated (in $\text{\AA}^2$) as follows ;

$$A = \frac{1}{\Gamma N 10^{-16}} \quad (23)$$

$$A_o = \frac{1}{\Gamma_{\max} N 10^{-16}} \quad (24)$$

Thus, the equilibrium model comprises the system of coupled non-linear algebraic equations represented by equations 14, 17, 19, 20, 22, 23 and 24.

3.2.4 Specification of the Regression Problem

In order to solve the model equations presented in the preceding subsection, use was made of regression techniques[43,44]. Firstly, we identify the variables of the regression problem. The independent variables which were also experimentally determined were C_{OH^-} , (V_w/V_o) , T and $(\text{CHA}_o)_o$. The dependent variable was Π , while the parameters to be estimated included K_{HA}^D and K_s . The third parameter n_c is associated with the variables K_p and W in the following manner:

1. K_p

Tanford[45] showed that for dilute solutions of saturated fatty acids in the range C8-C22, the partition coefficient was a linear function of chain length thus,

$$\begin{aligned} RT \ln \frac{X_w}{X_{\text{HC}}} &= -RT \ln K_p \\ &= 17807 - 3449n_c \end{aligned} \quad (25)$$

Equation 25 requires that all quantities are evaluated in SI units.

2. W

Similarly, Davies and Rideal[46] found that the energy of desorption was a linear function of the chain length of the acid thus,

$$W = n_c w \quad (26)$$

In equation 26, w , the energy of desorption per mole takes a value of 3385 J. Thus the variable common to both K_p and W is n_c , and it therefore becomes the third parameter to be estimated.

The constants of the regression problem were (B_2/B_1) and $\Gamma_{\max}$. The former has been shown by Davies and Rideal[46] to have a value of 20 $\text{\AA}$. For $\Gamma_{\max}$, we used the value of 45 $\text{\AA}^2$ per ion which van Voorst Vader[47] determined for the laurate ion at the heptane-water interface. Other

physical quantities such as D_c , k , ϵ and R were readily determined from the tables of physical property data that are available in standard handbooks[48,49].

3.3 Fractional Flow Analysis

3.3.1 Conservation Equations

In deriving the conservation equations applicable to the acidic crude/caustic system, the following assumptions have been made, viz:

1. The porous medium is isotropic, uniform and homogeneous.
2. The porous medium is totally water wet.
3. The displacement process is stable and takes place under isothermal conditions.
4. All fluids are incompressible and the solid matrix is not deformable.
5. Adsorption and hydrodynamic dispersion of chemical species are negligible.
6. Flow occurs in only one dimension and involves only water and oil (i.e. flow of emulsions is not considered).
7. Local chemical reaction equilibria exist at all points in the medium.

Going back to the interfacial reactions discussed in the preceding section, and noting that $C_{A-} \ll C_{OH-}$, we then substitute for C_{H+} (using equation 5) into equation 12. Neglecting C_{A-} , we can then solve for C_{OH-} in terms of C_{Na+} and the result is as follows:

$$C_{OH-} = 0.5 \left[C_{Na+} + \sqrt{C_{Na+}^2 + 4K_w} \right] \quad (27)$$

Making additional simplifying assumptions concerning the relative magnitudes of K_D and C_{NaA_w} , it can be shown[50] that $C_{HA_w} \ll C_{HA_o}$, so we may write the following;

$$C_{HA_o} = \left(\frac{K_p}{K_{HA}^D} \frac{K_w}{C_{OH-}} \right) C_{A-} \quad (28)$$

$$C_{NaA_o} = \left(\frac{C_{Na+}}{K_s} \right) C_{A-} \quad (29)$$

From equations 28 and 29, we can write an expression for C_{A-} as follows;

$$C_{A-} = \frac{C_{HA_o} + C_{NaA_o}}{\left(\frac{K_p K_w}{K_{HA}^D C_{OH-}} + \frac{C_{Na+}}{K_s} \right)} \quad (30)$$

Equations 27 and 30 coupled with equations 19, 20, 22, 23 and 24 are sufficient to solve for Π and hence σ in an iterative manner using the parameter values determined from the equilibrium IFT model.

3.3.2 Fractional Flow Equations

Following the treatment of Ramakrishnan and Wasan[50], we can write expressions for the superficial velocities of water and oil as follows:

$$v_w = (-kk_{rw}/\mu_w)(\delta p/\delta x) \quad (31)$$

$$v_o = (-kk_{ro}/\mu_o)(\delta p/\delta x) \quad (32)$$

Since the fractional flow of water is defined as;

$$f_w = v_w/(v_w + v_o) = v_w/v, \quad (33)$$

it follows therefore from equations 31 and 32 that

$$f_w = k_{rw}F_\mu/(k_{rw}F_\mu + k_{ro}) \quad (34)$$

where the viscosity ratio F_μ is given by:

$$F_\mu = \mu_o/\mu_w \quad (35)$$

In accordance with the relative permeability model developed by Ramakrishnan[51], the relative permeabilities of water and of oil can be represented as follows:

$$k_{rw} = 2S_w^{*2} \left\{ S^{*2}/2 - F_c/C^2 \left[\ln \frac{1+C-CS^*}{1+C} + \frac{1+C}{1+C-CS^*} - 1 \right] \right\} \quad (36)$$

$$k_{ro} = S_o^{*c2}(1 - S^{*2}) \quad (37)$$

The definition of the various saturation functions and other quantities appearing in equations 36 and 37 is as follows:

$$F_c = 0.3 + 0.7 \exp(-9500N_c) \quad (38)$$

The normalized wetting phase saturation is defined in terms of the wetting phase saturation as follows:

$$S_w^* = \frac{(S_w - S_{rw})}{(1 - S_{rw})} \quad (39)$$

The quantity C is defined in terms of the normalized maximum residual nonwetting phase saturation as follows:

$$C = (1/S_{ro,m}^{*o}) - 1 \quad (40)$$

The normalized disconnected nonwetting phase saturation is given by the following:

$$\begin{aligned} S_o^{*dc} = & [(1 + C - F_c) + C(1 + C)(1 - S_w^*)] \\ & - \left[(1 + C - F_c + C(1 + C)(1 - S_w^*))^2 + 4CF_c(1 + C)S_w^* \right]^{1/2} \\ & \div [2C(1 + C)] \end{aligned} \quad (41)$$

The value of S_o^{*dc} is constrained within the following limits, viz;

$$S_o^{*dc} \leq F_c/(1 + C) \quad (42)$$

The saturation variable S^* is given as follows:

$$S^* = 1 - S_o^{*c} = S_w^* + S_o^{*dc} \quad (43)$$

The capillary number is given by the following expression:

$$N_c = \left(\frac{v\mu_w}{\sigma} \right) \left[\frac{F_\mu}{(k_{rw}F_\mu + k_{ro})} \right] \quad (44)$$

Equations 36 through 44 provide an iterative process for calculating relative permeability values as a function of wetting phase saturation. With these relative permeability data, it is possible to predict fractional flow rates for water and for oil by the use of equations 34 and 35.

3.4 Solution of the Model Equations

3.4.1 The Equilibrium IFT Model

As was outlined earlier, the equilibrium IFT model consists of a series of coupled nonlinear algebraic equations. We seek a solution to these equations using the techniques of regression analysis. Thus, the problem becomes one of nonlinear parameter estimation for the three parameters namely K_s , n_c and K_{HA}^D . Two constants namely K_w and D_c are actually temperature dependent. Fortunately, we were able to obtain their values at each of the operating temperatures from the literature[48,49]. The well-known and powerful algorithm of Levenberg and Marquardt[52] was employed for this estimation problem. The particular package used was the IMSL routine ZXSSQ[53], a rather

convenient package in that analytical derivatives were not required. As in all parameter estimation problems, good initial guesses of the parameter values are essential. The method of trial and error solution through the model equations which we had used successfully in the past[42] was also employed here in order to get good initial parameter values.

Another important variable for which a good initial value was required was ψ_o . Again, the trial and error solution of the model equations was used to achieve this objective. For the precise determination of the value of this parameter for a given caustic concentration and temperature, a Newton-Raphson technique was used in a separate subroutine which iterated on equations 20 and 22 until a satisfactory convergence was obtained. The initial acid concentration present in the crude oil was calculated from the experimentally-measured total acid number. The actual programming task was straightforward once the experimental data and other constants had been supplied. The programming logic used was very similar to the procedure which was described previously[42].

3.4.2 The Fractional Flow Model

Since relative permeability depends on both saturation and capillary number, the conservation equations will have to be solved in order to obtain the interfacial tension corresponding to a given aqueous and oleic phase composition in the porous medium. Once the interfacial tension is known, as well as the flooding rate and viscosities of both the oil and the drive fluid, the iterative calculation of k_{rw} and k_{ro} can be carried out using equations 36 through 44. The limits for S_w were determined experimentally, and they were the complements of the residual oil saturation after secondary waterflooding and the final residual oil saturation following the injection of two pore volumes of the caustic solution.

The programming logic used for this calculation is as follows: For the given initial caustic concentration, C_{Na+} is known. Hence, C_{OH-} can be calculated using equation 27. Knowing C_{OH-} and the three equilibrium model parameters specified in the previous subsection, equation 30 can then be used to calculate C_{A-} . The calculation of Π follows directly from the solution of the coupled equations, namely equations 19 through 24. A separate Newton-Raphson routine was used for the calculation of ψ_o as previously indicated. The interfacial tension can be determined from the calculated surface pressure as follows:

$$\sigma = \sigma_o - \Pi \quad (45)$$

In this case, the reference interfacial tension σ_o corresponds to the value measured for the distilled water/crude oil system at the operating temperature.

Once the prevailing IFT has been calculated, the iterative solution of the fractional flow equations can start. A knowledge of the typical shape of the relative permeability-saturation curves is helpful. The value of k_{ro} usually exceeds that of k_{rw} at low values of S_w . For values of S_w close to 1, k_{rw} should exceed k_{ro} . Thus, depending on the wetting phase saturation, a judicious choice of initial guesses for the relative permeabilities must be made in order to get accurate converged values. A flexible convergence criterion (usually a difference of $10^{-3} - 10^{-5}$ in the relative permeability values obtained from two successive iterations) may be required. The iteration would start by evaluating the capillary number using equation 44. Then F_c , C , S_w^* , S_o^{*dc} and S^* are calculated in the indicated order. New values of k_{rw} and k_{ro} are obtained by solving equations 36 and 37. These new values are compared with the previous values and if they are not close enough, the new values are increased by a certain fraction (usually 0.1 to 0.5) of the difference between the new and the old values. The iteration is repeated several times until a satisfactory convergence is obtained. Once the oil and water relative permeabilities are known, the fractional flow of water is readily calculated by using equation 34.

4 RESULTS AND DISCUSSION

4.1 Screening of Alkaline Reagents - Task 2

Before we commenced the screening studies, we measured all pertinent physical and interfacial properties of the experimental crude oil. These measurements included density and viscosity at the six operating temperatures of 25, 35, 45, 55, 65 and 75°C, free water content, acid number and dynamic IFT against distilled water. Table 2 gives a summary of these measurements.

The acid number was measured by the Color-Indication Titration technique following ASTM D974-80 procedure. The viscosity of the crude at 25°C was 474 mPa.s. As can be seen from Fig. 3, the viscosity of the oil dropped to 32 mPa.s (about 6% of the value at 25°C) when the temperature was raised to 75°C. This dramatic drop in viscosity with modest temperature increases signifies that hot waterflooding would be beneficial for the reservoir. The IFT of the crude against water averaged about 27 mN/m. There was no significant effect on IFT due to temperature or the age of the interface. In view of these fairly-high tension values, hot waterflooding is not expected to effect any considerable reduction in residual oil saturation. Additional oil will be produced largely due to an improvement in oil mobility. The high acid number of the crude suggests that the addition of an alkaline reagent could be beneficial.

Table 4 gives the pH, density and viscosity of the alkaline solutions at the extremes of the working temperature range. In Table 4, we have presented data for three concentrations for each alkali. A total of eight concentrations in the range of 1.25 to 500 mM was involved in the study. All three physical properties decreased with an increase in temperature (see Table 4). For the solution viscosities, the decrease averaged about 40% for a change in temperature from 25 to 75°C. The viscosity also increased marginally with the increase in alkaline concentration. However, the density and viscosity values were not very different from those measured for distilled water under similar conditions. The relatively higher pH values measured for the orthosilicate solutions (in comparison to values determined for sodium hydroxide and sodium metasilicate systems) may be due to the formation of additional hydroxyl ions from the hydrolysis reactions involving the orthosilicate anion[16].

Figures 4 to 6 are comparative dynamic IFT plots for the three alkalis at 1.25, 25.0 and 125 mM respectively. These figures portray the effects of temperature and alkali type on dynamic IFT. At the low concentration of 1.25 mM (see Fig. 4), both NaOH and Na₂SiO₃ gave identical IFT

values of about 4 mN/m which were relatively unaffected by the age of the interface as well as by temperature. Quite surprisingly, sodium orthosilicate produced ultra-low tensions (below 10^{-2} mN/m) at 25°C. As shown in Fig. 4, a minimum in IFT of about 0.003 mN/m was obtained at an interface age of 1000 seconds. Beyond this contact time, the IFT increased marginally to an equilibrium value of 0.01 mN/m. For this same alkali at the higher operating temperature, the IFT was relatively unchanged at about 3.5 mN/m. Clearly, sodium orthosilicate was the most interfacially active alkali at this concentration.

In Fig. 5, the working alkaline concentration was 25 mM. The most interfacially active alkali was sodium hydroxide. The effect of contact time was more pronounced for all three alkalis than at the lower concentration of 1.25 mM. The IFT values obtained for all three alkalis were close at 25°C, with NaOH giving the lowest values. At 65°C, we found that the initial IFT for the NaOH/crude system was about 0.02 mN/m. However, this initial tension increased sharply to values near 1 mN/m after a contact time of 2000 seconds. This same behaviour was also manifested by sodium metasilicate. The increase in IFT for the orthosilicate system was more gradual. This trend in which the initial IFT dropped as temperature was increased was also observed by Babu et al.[24] as well as Mehdizadeh and Handy[25]. The decrease in IFT at higher temperature favours oil recovery, but the rapid increase in the same IFT at extended contact times is undesirable. At the working alkaline concentration of 125 mM, we found IFT-time trends similar to those obtained at 25 mM concentration. Again, NaOH would be the alkali of choice (see Fig. 6). The disparity in tension values for the three alkalis at both 25 and 65°C was considerably reduced.

In general, the average IFT values for all three alkalis increased at higher operating temperatures irrespective of the working concentration. However, the optimum concentration of the alkali tended to shift to higher values as the temperature was increased. This was more pronounced for the silicates and it may not be apparent from Figs. 4-6. The only way that one could detect this variation in the optimum concentration was by carefully examining the dynamic IFT data at all eight working concentrations and for all six operating temperatures. In the case of NaOH, the optimum concentration was relatively unchanged at 12.5 mM for all operating temperatures. However, the tension values obtained at 25 mM were close to values measured at 12.5 mM. For sodium metasilicate, the optimum concentration at 25°C was 2.5 mM. At higher temperatures, the optimum concentration shifted to 12.5 mM. As we saw in Fig. 4, the optimum for sodium orthosilicate at 25°C was 1.25 mM. At higher temperatures, 2.50 mM became the optimum concentration. The

possibility for the optimum alkaline concentration to shift to a higher value when the operating temperature is increased must be taken into account in the design of an alkaline flood. Even if potential losses to the reservoir from adsorption and ion exchange with matrix minerals were to be discounted, the potential shift in optimum would compel the reservoir engineer to use a higher alkaline concentration than what might seem to be the optimum from IFT studies conducted at one temperature alone.

4.2 Screening of Surfactants and Cosurfactants - Task 3

Three surfactants namely Petrostep B-100, Petrostep B-110 and Petronate L were screened at four concentration levels and three temperatures. The concentrations used were 0.1, 0.5, 1.0 and 2.0% by weight respectively, while the operating temperatures were 25, 45 and 65°C. The objective was to determine which surfactant and which concentration produced the minimum in IFT against the target crude. Surfactant concentrations used in micellar processes typically exceed 2.0% by weight. Lower concentrations would have to be used in SA formulations if the overall process is to remain economically justifiable. It turned out that no appreciable improvement in interfacial activity was obtained at surfactant concentrations above 0.5% as far as the Court crude was concerned.

Figs. 7-10 are the dynamic IFT plots for all three surfactants at concentrations of 0.1 and 0.5% by weight and temperatures of 25 and 65°C respectively. The IFT of the Petronate L and Petrostep B-100 surfactants (in the presence of the Court crude) was only marginally affected by contact time. Figures 8 to 10 show that the IFT of the Petrostep B-110/Court crude system was significantly influenced by contact time. For this surfactant, the initial tension was about two times that exhibited by the other surfactants. However, the equilibrium values were much closer for all three surfactants. The interesting aspect about the behaviour of these surfactants was the tendency for the IFT to decrease with contact time. The average tension values were much higher than those obtained with the alkaline solutions alone. However, it appeared that the surfactants would be able to moderate the interfacial activity of the alkaline solutions by reversing the trend of increasing IFT with contact time.

In the next phase of the study, we attempted to improve the performance of the surfactant solutions by the addition of cosurfactants. Again, we tried to use conventional cosurfactants such as fatty alcohols (butanol and hexanol), but no significant improvement was realized. In the end, we turned to the two lignosulfonates, namely Marasperse N-22 and C-21, that we had used

successfully in previous studies[30] to enhance the interfacial activity of petroleum sulfonates by as much as 40 to 80%. We screened the two lignosulfonates at four concentration levels namely 0.05, 0.1, 0.5 and 1.0% by weight. In all cases, Marasperse C-21 consistently yielded the lower tension values. Tensions at the higher concentration range were about 30% lower than at the lower range of lignosulfonate concentration. Again the optimum concentration was found to be 0.5%. In Figs. 11 and 12, we plotted the dynamic IFT data for 0.1% (by weight) Petrostep B-100 containing varying concentrations of lignosulfonates. A comparison of Figs. 7 and 8 with Figs. 11 and 12 clearly demonstrates the improvement in the interfacial activity of the surfactant following the addition of lignosulfonates. The average IFT for the surfactant solution alone was about 8 mN/m. In Fig. 11, we find that at a lignosulfonate concentration of 0.1% (by weight), the average IFT was down to about 1.5 mN/m. The same improvement was also recorded at the higher operating temperature of 65°C.

The next phase of the study featured the formulation of alkaline-surfactant mixtures containing lignosulfonates as cosurfactants. First we kept the surfactant-cosurfactant concentrations at 0.1 and 0.5% by weight respectively, while the NaOH concentration was varied between 25 and 250 mM. All dynamic IFT measurements were carried out at temperatures of 25, 45 and 65°C respectively. The interfacial tension behaviour of these ternary systems at 25 and 125 mM NaOH concentration levels is as shown in Figs. 13 through 15. In Figure 13, we find that the addition of the surfactants produced much higher tensions compared to 25 mM NaOH alone. In Figure 15, the presence of the surfactants reversed the trend in which the IFT was increasing sharply with extended contact time. However, the initial IFT of the mixture system was still unacceptably high.

At this stage, we decided to lower the complexity of the SA formulations from a ternary to a binary system wherein either surfactant B-100 or lignosulfonate C-21 was added but not both of them. This amounts to a limited decoupling of the ternary SA formulations. Since lignosulfonates are actually high molecular weight polyelectrolytes, we considered that the presence of such a species could interfere with the accumulation of the much more surface-active soap anions and B-100 sulfonates at the oil/water interface. These repulsive forces would be largely steric and coulombic in nature. On the basis of this assertion, we developed binary SA systems and the highlights of the IFT studies using such solutions are shown in Figs. 16 to 18. These plots clearly show that the IFT of the alkali/C-21 systems were consistently higher than those of NaOH alone and of the NaOH/B-100 systems. The ability of B-100 when added to the alkaline solution to

sustain a continual drop in IFT even at higher temperatures and long contact times is evident in these plots. Thus the much desired improvement in the interfacial activity of the alkaline solutions has indeed been achieved.

4.3 Screening of Polymers - Task 4

The five polymers which were used in this phase of the study can be classified as follows:

- (i) two non-ionic polymers namely Xanthan gum and polyethylene oxide. The latter had an average molecular weight of four million while that of the former was unspecified.
- (ii) three polyacrylamides identified as (a) a non-ionic product with a molecular weight of five to six million, (b) an anionic product of unspecified molecular weight, and (c) a cationic product with a molecular weight in the range of seven to nine million.

The suppliers of these polymers have been identified in Table 1. The objective of these MAP-type formulations was to increase the bulk viscosity of the SA systems developed from the earlier tasks without incurring an appreciable loss in the interfacial activity of the composite system. Thus, phase compatibility and system stability were important criteria for choosing a suitable polymer. Preliminary experiments, however, indicated that aging affected the rheological behaviour of the polymeric solutions. Accordingly, we had to alter our investigative strategy in order to explore this rather interesting phenomenon.

4.3.1 The Xanthan Gum System

This polymer is widely used in enhanced oil recovery due mainly to its good salinity tolerance and its good thermal stability. The polymer is however known to be susceptible to bacterial degradation. What is not well known is its performance in high pH environments. The viscosity of a 0.2% (by weight) solution of the polymer was 387 mPa.s at 6 rpm and only 81 mPa.s at 60 rpm (both measurements being carried out at 25°C). With 0.1% polymer solution, the corresponding figures were 105 and 35 mPa.s respectively. These solutions retained their viscosities for the one week that we worked on the Xanthan gum system. When we incorporated the polymer in the NaOH/B-100 formulations, the viscosity of the mixture dropped considerably. For example, the viscosities of fresh solutions containing 12.5, 25 and 125 mM NaOH in the presence of 0.1% B-100 and 0.2% Xanthan gum (measured at 6 rpm and 25°C) were 176, 178 and 193 mPa.s respectively. After aging for five days, the same solutions had viscosities (measured at 65°C) of 14, 10 and 32 mPa.s

respectively. Despite this severe loss in viscosity, the presence of the polymer did not adversely affect the interfacial activity of the overall system.

4.3.2 The Polyox System

Polyethylene oxide(Polyox) is not a commonly-used polymer in enhanced oil recovery practice. However, being non-ionic, we thought that its structure could possibly promote a favourable association between the in-situ formed soap anions and the surfactant species. We used this polymer at two concentration levels, namely 0.8 and 0.5% by weight. Polyox is very strongly pituitous and at the same time very susceptible to auto-oxidation in aqueous media. It is therefore recommended[54] that small quantities of lower alcohols be added to the polymer solution as a stabilizing agent. For this purpose, we used 4% and 2% by volume of iso-propanol respectively. A solution containing 0.8% by weight of the polymer in water had a viscosity at 6 rpm and 25°C of 750 mPa.s, while at 60 rpm the viscosity had dropped to 275 mPa.s. In an alkaline solution containing respectively 12.5, 25 and 125 mM NaOH with 0.1% B-100, the addition of 0.8% Polyox resulted in solution viscosities (at 6 and 60 rpm, 25°C) of 710, 250; 600, 218; 555, 215 mPa.s respectively. Since the decrease in viscosity was quite minimal, we proceeded to study the rheology of the solutions as a function of age. After 30 days, the polymer solutions had suffered no appreciable loss in viscosity, while the alkali-surfactant-polymer formulations witnessed some reduction in viscosity ranging from 10 to 30%.

The pituitous nature of the polymer was not a factor in its rheological behaviour. Rather, it affected the measurement of dynamic IFT. This property prevented the oil droplet rotating in the capillary tube of the tensiometer from responding instantly to changes in the boundary tension. This has been referred to as the Relaxation Effect by Neale et al.[55]. Under these circumstances, it was impossible to obtain true tension values. The lower the polymer concentration, the less severe was the stringiness of the solution. Consequently, the lower were the apparent tension values. The fact that the polymer did not lose its viscosity significantly in the high pH environment makes it a good potential candidate for polymer augmented-caustic waterflooding.

4.3.3 The Nonionic Polyacrylamide System

The working concentration used for this polymer was 0.5% by weight. N-butanol was added in an amount corresponding to 0.5% by volume as a dispersing/stabilising agent. This polymer exhibited

a rather interesting rheology that was a strong function of NaOH concentration as well as of the age of the solutions. Traditionally, anionic polyacrylamides are thought to be the most compatible with highly alkaline solutions. This nonionic polyacrylamide outperformed the anionic one at all NaOH concentrations and various operating temperatures. First, we studied the effect of the addition of the polymer on the interfacial tension behaviour of the alkali-surfactant system. The age of the solution at the time this study was done was seven days. Figures 19 to 23 summarize the results that were obtained. In general, the addition of the polymer resulted in initial tensions that were higher than those measured for the NaOH and NaOH/B-100 systems. However, the equilibrium tension values fell below those of the SA systems at all operating temperatures. We attributed the higher initial tensions to the relaxation effect discussed in the previous subsection. The disparity between the IFT of the SA system and those of the PSA systems was small in general. The addition of the polymer did not appear to have adversely affected the interfacial activity of the composite formulation.

The rheology of the PSA systems was studied for an aging period of 70 days. The effect of NaOH concentration and solution age can be seen from Fig. 24. For all NaOH concentrations, the viscosity continued to increase with the age of the solution. However, the most significant increases were recorded at a caustic concentration of 25 mM NaOH. The worst case was the solution that contained 125 mM NaOH. Even for the 125 mM solution, the viscosity attained after 70 days was about seven times the value measured for the polymer solution alone. The polymer solution alone suffered no detectable loss in its viscosity after the 70 days aging period. As for the PSA solution containing 25 mM NaOH, its viscosity after 70 days reached 1300 mPa.s (about 40 times that of the alkali-free polymer solution). Polyacrylamides are believed to hydrolyze in a high pH environment with the formation of carboxylate anions. The repulsion between these charged species causes the polymer chain to expand and this leads to an increase in viscosity. The degree to which the polymer expands depends on its molecular weight and the extent of hydrolysis. Thus, NaOH levels of 125 mM and higher favour less chain expansion which gives lower viscosities when compared with solutions containing smaller amounts of NaOH.

4.3.4 The Anionic Polyacrylamide System

Anionic characteristics are incorporated into the polymer either by partial hydrolysis or by the addition of a co-monomer such as acrylic acid. The Calgon 300 polymer which was used in this

study is believed to contain acrylic acid as the co-monomer. A fresh solution containing only 0.1% by weight of the polymer had a viscosity (measured at 6 rpm and 25°C) of 700 mPa.s. After aging for 50 days, the viscosity of the solution had dropped by only 10%. A significant loss of viscosity occurred when the polymer was added to the NaOH/B-100 formulations. The loss of viscosity was more severe as the alkalinity of the solution increased. The effect of NaOH concentration and aging on the PSA systems containing Calgon 300 anionic polyacrylamide is shown in Fig. 25. No noticeable adverse effect on interfacial activity was manifested for the PSA systems containing Calgon 300.

4.3.5 The Cationic Polyacrylamide System

This product (supplied by Betz Incorporated) was also a high molecular weight polyacrylamide. The viscosity of a 0.2% solution of the polymer in water was about 500 mPa.s at 6 ppm and 25° C. After 50 days, the viscosity of this solution had dropped to 325 mPa.s (measured under similar conditions). When the polymer was added to the NaOH/B-100 systems, the viscosity of the resulting solutions was lower than the value determined for the polymer solution alone. For example, fresh solutions containing 12.5, 25 and 125 mM NaOH respectively in the presence of 0.1% B-100 and 0.2% of the polymer had viscosities (measured at 6 rpm and 25°C) of 135, 100 and 60 mPa.s respectively. After 50 days, the same solutions had viscosities measured under similar conditions of 500, 350 and 110 mPa.s respectively. The viscosity of these PSA systems thus increased with age, but the increase was less pronounced in solutions containing higher amounts of alkali. Again, no adverse effects on the interfacial activity of the alkali-surfactant systems were manifested when the polymer was added at the 0.2% concentration level.

4.4 Linear Displacement Tests - Task 5

4.4.1 Water and Base Alkali Runs

These displacement tests were carried out at three different temperatures namely 25, 45 and 65°C respectively, and they were intended to serve as a basis for proper evaluation of the performance of the newly developed SA and PSA systems. The results of the alkali screening studies indicated that sodium orthosilicate was not more surface-active than the other two alkalis. This alkali was therefore not used in the displacement tests. A summary of all tests carried out with the alkaline

solutions is presented in Table 5. The term 'Tertiary Oil Recovered' which appears in this table refers to the percentage of residual oil (remaining after the secondary waterflood) that was recovered during the tertiary stage. The alkaline solutions as well as the SA and PSA formulations were all injected in the tertiary mode. The injection rate was kept constant for all runs at 3.99 mL/min (2.7 m/day). Figs. 26 and 27 depict oil recovery histories at 25 and 65°C respectively for the runs conducted with water and with three NaOH solutions. Recovery histories for sodium metasilicate at similar temperatures and identical compositions did not differ substantially from those of NaOH (see Table 5). The cumulative oil recovered after the injection of three pore volumes of water at 25° and 65°C respectively was 24% and 37%. The amount of additional oil recovered at the higher flood temperature was quite significant. Furthermore, the data presented in Table 5 indicate that over 80% of the waterflood oil recovery occurred during the injection of the first pore volume of the drive fluid. Thus, commencing the caustic flood after injecting one pore volume of water ensured that the full potential of the waterflood was exploited.

Fig. 26 (see also Table 5) clearly shows the superior oil recovery potential of the NaOH solutions over water at 25°C. Comparing the oil recovery efficiencies of the various alkaline solutions, we could see that the most effective concentration was 12.5 mM, followed closely by 25 mM. This was true for both NaOH and sodium metasilicate and it is consistent with the results of the dynamic IFT screening studies. At 65°C, the alkaline solutions failed to recover additional oil beyond the value obtained with water alone. This was rather surprising given the fact that the IFTs of these solutions against the Court crude were generally below 1.0 mN/m. For the caustic floods conducted at the lower temperature, we observed an increase in the pressure drop across the porous medium as soon as the injection of the alkaline solution commenced. This relatively high pressure drop persisted for a long time during which mostly neat oil was produced. For the 65°C floods, no appreciable increase in pressure drop through the bed was observed. Most of the oil produced during the injection of the alkali was in the form of an emulsion. The oil content of the emulsion decreased continually as the injected fluid volume increased. Comparing the oil recovery figures for sodium hydroxide and sodium metasilicate (Table 5), we find that the latter performed marginally poorer. The effluent during the silicate floods was always turbid. This could be associated with the precipitation of siliceous material formed by the hydrolysis of the silicate anion. The presence of these colloidal particles could have prevented the oil entrained in the produced oil-in-water emulsions from coalescing into bigger droplets with the possibility of forming an oil bank.

4.4.2 Displacement Tests with SA Systems

For these runs, only NaOH was used as the test alkali in admixture with Petrostep B-100. Table 6 provides a summary of the results of these runs. Comparing these oil recovery data with those given in Table 5, it is quite apparent that the SA formulations failed to recover as much oil as the base alkaline solutions. This runs contrary to the dynamic IFT data for the SA systems where a significant enhancement in interfacial activity was clearly manifested. The common feature of these runs was the relatively small quantity of neat oil produced during the injection of the alkali-surfactant solutions. In nearly all cases, oil was produced in an emulsified form both as water-in-oil and oil-in-water emulsions. One plausible theory to account for the poor performance of these SA systems is that chromatographic separation occurred between the in situ-formed soap anions and the injected alkylaryl sulfonate, with the latter as the lead species. Since these species contacted the oil first, the relatively higher tensions prevented a significant amount of the residual oil from being mobilized. Phase incompatibility does not appear to be the cause of this separation since no visible precipitation was observed even after the solutions were left to stand for several weeks.

4.4.3 Displacement Tests with Polymer and PSA Systems

Two polymers, namely polyethylene oxide and nonionic polyacrylamide (SP2 PAM), were used in these displacement runs. The polymer solutions alone were employed as the tertiary drive fluid at each of the three working temperatures. These runs served as the basis for the evaluation of the PSA systems. The summary of the runs involving both Polyox and SP2 PAM is presented in Table 7. Figs. 28-31 give the production histories at 25 and 65°C respectively for both polymer systems. The amount of tertiary oil recovered has been used as the main criterion for assessing the performance of the various formulations. However, this criterion does not provide a complete evaluation of the oil recovery potential of each system.

In Fig. 28, we find that the introduction of NaOH and surfactant B-100 resulted in additional oil recovery (over that produced by 0.5 weight% Polyox) of about 25% at 25°C. No significant additional oil was produced by the PSA solutions containing Polyox at higher temperatures (see Table 7). Table 7 also gives the approximate oil/water viscosity ratio, which for the Polyox systems decreased from about 3.5 at 25°C to about 1.5 at 65°C. Despite this reduction in the viscosity ratio, only the additive-free polymer solutions recovered more oil at higher temperatures. Another factor which complicates the interpretation of these tests is the variation in the final pore volumes of

fluids injected. This variation was brought about by the increasing degree of permeability reduction as more polymer solutions were injected. An examination of the nature of the sand forming the porous medium at the end of the flood showed clearly that the permeability of the medium had been reduced considerably by the flow of the polymeric fluids. By comparing the ratio of water to oil in the effluent (WOR) at the termination of the run, we found that the reduction in permeability affected the flow of water more severely than that of oil. In the case of Polyox, the WOR varied from about 8 for polymer solutions alone to 3 for the PSA formulations. The WOR values at the termination of the SA runs were all above 12, often reaching 100 in the worst cases.

In Figs. 30 and 31, we find that the recoveries obtained with the PSA composite systems containing SP2 PAM were about 20% higher than the values obtained with the polymer solutions alone at both 25 and 65°C. The viscosity of the 0.5% SP2 PAM solutions was 40 mPa.s at 25°C and 25 mPa.s at 65°C. The viscosities of the PSA solutions were 5 to 10 times the values measured for the polymer solutions alone. This accounts for the consistently higher recovery given by the PSA systems. The most surprising aspect was the failure of the solution containing 25 mM NaOH to recover appreciably more oil than the other PSA solutions despite the fact that its viscosity was 1.5 to 2.5 times the value of the other solutions containing more or less NaOH (see Table 7). At this NaOH concentration, we find that the viscosity ratio was below 1.0 and indeed fell to 0.1 at 65°C. One indication that these PSA formulations do indeed possess the potential to recover 100% of the residual oil is given by the WOR. The range of these values for the SP2 PAM systems was about 3 to 0.6, with the lower values predominating at higher temperatures.

There were some production problems which were posed by the injection of the PSA systems. The most dominant was the decline in production rate soon after breakthrough of the chemical system. In order to compensate for this loss in injectivity in a real reservoir, the throughput of the dosing pump would have to be increased. The other problem which we observed was that following the breakthrough of the PSA system, oil was produced mostly in an emulsified form. Additional downstream facilities would be required in order to handle this potentially difficult emulsion problem.

The results presented in Table 7 indicate that polymer flooding using Polyox would be potentially beneficial. It is important to note that these displacement tests were conducted at relatively high flooding rates. The typical flow rate in a real reservoir is about 0.3 m/day compared to the flood rate of 2.7 m/day used for these tests. The total permeability of the medium of 147 darcies

is also high in comparison with typical reservoir permeabilities ranging from 100 to 1000 millidarcies. The combination of high permeabilities and flooding rates used in the runs would lead to the dominance of viscous rather than capillary forces. This condition was quite favourable to the polymer floods. Under actual reservoir situations, capillary forces would be more important and we would therefore expect the PSA solutions to perform much better. The decision as to which polymer would ultimately be used for a given reservoir would depend on the prevailing salinity and the proposed flood temperature. For applications at temperatures above 70°C, particularly for crude viscosities of up to 1000 mPa.s at reservoir conditions, polyacrylamide would appear to be a better choice than Polyox. With either polymer, the use of an appropriate stabilizer is warranted.

4.5 Mathematical/Numerical Simulations - Task 7

4.5.1 Equilibrium IFT Model

The experimental data which were used for the solution of the equilibrium model equations have been listed in Appendix A for three temperatures namely, 25, 45 and 75°C respectively. Parameter estimates were obtained at all six operating temperatures using nonlinear least squares regression analysis. These parameter values were those that gave the least sum of squares of residuals (SSR) in accordance with the Marquardt algorithm[52]. The final parameter values have been listed in Table 8. At 25°C, we obtained a K_{HA}^D value of 8.0×10^{-7} mol. m^{-3} . This was well within the range of $10^{-7} - 10^{-9}$ mol. m^{-3} which was suggested by deZabala[56] as being the most probable range of the ionization constant of crude oil acids. Ramakrishnan and Wasan[41] obtained a value of 2.8×10^{-7} mol. m^{-3} for the acid ionization constant, and a K_a value of 0.175 mol. m^{-3} , with 13 as the number of CH_2 groups for a sample of Long Beach California crude. These values compare very well with the figures we determined for the Court crude at ambient conditions.

No previous attempts have been made to predict the values of these equilibrium constants at temperatures above ambient conditions, although such data are necessary for the design of alkaline waterfloods at elevated temperatures. The data shown in Table 8 clearly indicate an increase in K_{HA}^D value as temperature increased. The greatest increase in K_{HA}^D was recorded when temperature increased from 25 to 55°C. In this temperature range, the ionization constant increased by two orders of magnitude. Thereafter, the increase was within an order of magnitude. This again lends credence to our earlier assertion that alkaline flooding would be more effective at moderate temperatures than at much higher values such as would be encountered with the use of steam.

No consistent pattern was manifested by either the K_s or CH_2 values (see Table 8). It should be remembered that K_s is actually a product of the dissociation constant for the sodium soap (NaA_w) and the partition coefficient for the transfer of NaA_w to the oleic layer in the form of NaA_o . While the dissociation constant might be expected to increase (or decrease) with temperature, the partition coefficient could be weakly dependent on temperature, or its variation with temperature could be opposite that presented by the dissociation constant. In either case, no established variation would be manifested. The number of CH_2 groups was not expected to be temperature sensitive, and as can be seen from Table 8, these values were relatively unchanged.

4.5.2 Temperature Correlation Coefficient for K_{HA}^D

In view of the trend established in Table 8 for the variation of K_{HA}^D values with temperature, we attempted to determine a correlation that would represent this relationship. In line with the established dependence of K_w on temperature[49], we sought an Arrhenius-type relationship as follows:

$$-\log K_{HA}^D = Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 \quad (46)$$

where,

$$X_1 = 1/T, X_2 = 1/T^2 \quad (47)$$

The above equations represent a second degree polynomial in $1/T$ for pK_{HA} . The task then is to obtain the best estimates for the coefficients β_0 , β_1 and β_2 by means of least squares regression. This was easily done with the aid of the REG routine in SAS software packages[57]. The estimates of the correlation coefficients are given in Table 9 along with the standard errors associated with each estimate. An attempt was made to raise the degree of the polynomial to three, but the correlation between the coefficients was very high and that led to equally high standard errors in the estimates. In Fig. 32 we plotted values of the actual and predicted pK_{HA} as functions of $1/T$. The agreement between the actual and predicted values was satisfactory over the operating temperature range. In Fig. 33, we have also plotted the residual (actual-predicted) pK_{HA} values as a function of $1/T$. Again, there is no obvious trend in the residuals which might suggest any inadequacy in the model. Thus, the correlation relationship between temperature and K_{HA}^D is as follows:

$$\log K_{HA}^D = 169 - 1.08 \times 10^5(1/T) + 1.8 \times 10^7(1/T^2) \quad (48)$$

4.5.3 Fractional Flow Analysis

We solved the fractional flow equations for the case of 12.50 mM NaOH displacing Court crude at 25°C. The alkaline solution was injected as a tertiary fluid immediately after the injection of one pore volume of water. The experimentally determined fluid saturations at the beginning and the end of the flood were 0.18 for S_{rw} and 0.339 for $S_{r,oc}$. The prevailing capillary number N_{ca} was calculated to be 5.88×10^{-4} . Fig. 34 depicts the variation of the water and oil relative permeabilities with the wetting phase saturation under primary imbibition. The relative permeability of water started at a low value of 2.29×10^{-4} , but at the termination of the run it had climbed to 0.12. On the other hand, the relative permeability of the oil was very much greater than that of water until the very end of the flood. This situation was very favourable for oil recovery, which may account in part for the high recovery values obtained under these conditions. Using the calculated relative permeability values, it was then possible to predict the fractional flow rate of water as a function of wetting phase saturation. This relationship is shown in Fig. 35. The fractional flow rate of water increased markedly in the saturation range of 0.36 to 0.43. This suggests that towards the end of the run essentially only water would be produced. That was the case with the alkaline floods and we evaluated WOR values in the range of 30 to 100 towards the end of the run.

5 CONCLUSIONS

The following conclusions can be drawn from the work carried out under this contract:

1. Sodium hydroxide, sodium metasilicate and sodium orthosilicate solutions all yielded low interfacial tensions when contacted with the Court crude. The average IFT values measured at any given alkaline concentration increased with an increase in temperature.
2. The most surface active alkali for the target crude was sodium hydroxide followed by sodium metasilicate. The optimum NaOH concentration was 12.50 mM while the optimum temperature was 25°C.
3. The silicates exhibited an optimum concentration near 2.50 mM at low temperatures but this shifted to higher values as the operating temperature was increased.
4. The addition of small quantities of a conventional surfactant resulted in an improvement of the surface activity of the base alkaline solutions. The improvement was more pronounced at higher alkaline concentrations where the tendency for the IFT to increase with contact time was reversed.
5. Xanthan gum when added to a solution containing NaOH and surfactant B-100 improved the interfacial efficacy as well as the viscosity of the system. However, this polymer could not tolerate high pH and the mixture lost its viscosity within a few days.
6. An anionic polyacrylamide used as a thickener for the surfactant-alkali formulations exhibited a gradual but significant loss in viscosity with the age of the solution.
7. Polyethylene oxide maintained its viscosity in the alkaline-surfactant solutions even after two months of aging. Another polymer that performed well in the high alkaline environment was nonionic polyacrylamide.
8. About 12% more oil was recovered by waterflooding at 65°C than at 25°C.
9. Flooding with alkaline solutions was favourable at concentrations of 12.5 and 25 mM NaOH and at temperatures below 45°C.

10. Alkaline solutions containing surfactant B-100 and Polyox recovered about 80% of the residual oil following secondary waterflooding at 25°C. Tertiary oil recovered at higher temperatures was in the range of 70 to 85%.
11. The use of polymer solutions alone improved waterflooding oil recovery by between 40 to 60%. The use of Polyox resulted in the higher oil recovery values while polyacrylamide yielded additional recovery values close to 40%.
12. The viscosity of alkaline solutions containing B-100 and anionic polyacrylamide increased significantly with the age of the solution. The viscosity of a solution containing 25 mM NaOH, 0.1% B-100 and 0.5% polyacrylamide increased to 1300 mPa.s after an aging period of two months. The increase in viscosity with age was less for the solution containing 125 mM NaOH.
13. An equilibrium IFT model has been proposed which is capable of accounting for the behaviour of acidic oils in contact with alkaline media. The pertinent interfacial parameters for the Court crude/NaOH system have been identified and evaluated.
14. Using this model, we were able to predict the IFT values that would prevail in a typical caustic flooding situation.
15. Using the calculated equilibrium model parameters, we have developed a fractional flow model which can predict the fractional flow rate of water in the porous medium as a function of wetting phase saturation.
16. The Court heavy oil reservoir should be considered for hot waterflooding or hot polymer flooding.
17. The use of alkaline reagents and alkaline solutions containing surfactants and polymers would be potentially beneficial at flood temperatures ranging from 25 to 65°C.

6 RECOMMENDATIONS FOR FUTURE WORK

Before any of the chemical enhanced oil recovery processes that we have explored in this project can be implemented in the field, additional laboratory work will needed, as follows:

1. Studies of the interfacial activity and phase compatibility of the SA, CSSA and PSA systems in actual reservoir brine (connate water) as a function of alkaline concentration and temperature.
2. Adsorption and retention studies using cores prepared with actual reservoir sands and containing real reservoir fluids. The effects of temperature on adsorption and on the retention of alkalis, surfactants and polymers should also be investigated.
3. Additional displacement studies should be conducted with natural cores at typical reservoir pressures and various temperatures.

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8 NOMENCLATURE

A	surface area per molecule, $\text{\AA}^2$
A_o	minimum surface area per molecule, $\text{\AA}^2$
B	adsorption or desorption rate constants
c, C	molar concentrations
D_c	dielectric constant of water
f	surface coverage by the adsorbed species
F	viscosity ratio (oil to water)
k	Boltzmann constant
k_{ro}	relative permeability to oil
k_{rw}	relative permeability to water
K_{HA}^D	acid dissociation constant
K_D	salt distribution ratio water/oil
K_p	acid distribution ratio oil/water
K_s	equilibrium constant associated with species, NaA
K_{s1}	inactive soap dissociation constant
K_{s2}	inactive soap distribution ratio
K_w	ionic product of water
n_c	number of CH_2 groups in the hydrocarbon chain
N	Avogadro number
N_{ca}	capillary number as $N_{ca} = \frac{v\mu_w}{\sigma}$
R	universal gas constant
S	phase saturation
S^*	normalized saturation
T	temperature, K

v	velocity
V	phase volume, droplet volume
w	desorption energy per mole, per CH_2 group
W	total energy of desorption per mole
X	independent variables of the correlation model
Y	dependent variable of the correlation model
z	ionic valency

SUBSCRIPTS and SUPERSSCRIPTS

c	connected
dc	disconnected
HA	acid species
m	maximum
NaA	inactive soap species or salt
o	initial state, oleic phase
ro	residual oil
rw	residual water
s	sub-layer, steric
w	water, aqueous phase

GREEK LETTERS

β	correlation parameter
ϵ	electronic charge
Γ	surface concentration of adsorbed species
Γ_{max}	saturation adsorption, mole/ m^2
μ	dynamic viscosity
σ	interfacial tension, mN/m

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TABLE 1: SPECIFICATION OF REAGENTS USED

NAME	SPECIFICATION	SUPPLIER
Sodium hydroxide	'Aristar' grade NaOH Pellets contains less than 1% Na_2CO_3	BDH Chemical Company
Sodium metasilicate	Certified grade $\text{Na}_2\text{SiO}_3 \cdot 9 \text{H}_2\text{O}$ Powder	Fisher Scientific Company
Sodium Orthosilicate	Prepared by mixing stoichiometric amounts of NaOH with $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	-
Petrostep B-100	Medium molecular weight alkylaryl sodium sulfonate contains 60% actives	Stepan Chemical Company
Petrostep B-110	High molecular weight alkylaryl sodium sulfonate contains 50% actives	Stepan Chemical Company
Petronate L	Oil Soluble alkylaryl natural petroleum sulfonate, mol. wt 415-430, sulfonate (%): 61-63	Witco Chemical Corporation
Xanthan Gum	non-ionic polysaccharide	Aldrich Chemical Company
Polyethylene Oxide	non-ionic polymer average molecular weight of 4 million	Aldrich Chemical Company
Polyacrylamide	Non-ionic nominal mol. weight of 5 to 6 million	Scientific Polymer Products (Sp^2) Inc.
Betz 1160X Polyacrylamide	Cationic polyacrylamide mol. weight 7 to 9 million	Betz Inc.
R-300	High molecular weight anionic polyelectrolyte	Calgon Corporation
Marasperse N-22	Sodium based lignosulfonate, $[\text{Na}^+] = 6.7\%$ by weight	American Can. Company
Marasperse C-21	Calcium based lignosulfonate $[\text{Ca}^{2+}] = 4.0\%$ by weight	American Can. Company

TABLE 2: RESERVOIR AND CRUDE OIL CHARACTERISTICS

Name of Crude: Saskoil Canadian Reserve Court

Well location: 4-25-33-28 W3M

Formation: Unconsolidated Sparky and Bakken Sands

Crude Oil Properties:

Gravity: 17.7° AP1

Density at 25°C: 945.1 kg/m³

Density at 75°C: 918.4 Kg/m³

Water in crude: < 0.5% (by volume)

Sulphur in crude: 2.8% (by weight)

Acid Number: 1.88 (mg KOH/g crude)

Interfacial Tension between crude oil and distilled water:

at 25°C - 45°C: 26-31 mN/m (decreasing slightly with contact time)

at 55°C - 75°C: 23-30 mN/m (decreases slightly with contact time)

Table 3. Characteristics of the Porous Medium

Type:	Unconsolidated Accusand meeting ASTM C-190 Specifications
Sand producer:	Unimin Corporation, Minnesota
Local supplier:	Canada Wide Scientific Company, Ottawa, Ontario
Bed porosity:	0.32-0.33
Total permeability (water at 23°C):	147 darcies
Mean particle diameter:	599 µm
Sand grain density:	2.63 kg/L
Volume of core holder:	1.3 x 10 ⁻³ m ³
Length of core holder:	0.61 m

TABLE 4: PHYSICAL PROPERTIES OF ALKALINE SOLUTIONS							
Reagent	Concentration (mM)	PROPERTY VALUES					
		PH at		Density Kg/m ³		Viscosity	mPa.s at
		25°C	45°C	25°C	75°C	25°C	75°C
NaOH	1.25	11.1	10.6	997.1	975.1	0.8905	0.3969
	25.0	12.3	11.8	998.1	976.3	0.8961	0.4000
	250.0	13.1	12.4	1007.8	991.0	0.9859	0.4188
	500.0	13.3	12.6	1018.0	1001.0	1.1280	0.4203
Na ₂ SiO ₃ .9H ₂ O	1.25	11.0	*10.7	997.4	978.6	0.8924	0.3717
	25.0	12.2	*12.0	1000.1	981.6	0.9025	0.3752
	250.0	12.9	*12.7	1026.4	1006.9	1.0314	0.4199
	500.0	13.1	*12.9	1054.3	1034.2	1.1764	0.4731
Na ₄ SiO ₄	1.25	11.6	10.9	998.3	979.9	0.8182	0.3586
	25.0	12.7	12.1	1003.3	984.9	0.8434	0.3624
	250.0	13.4	12.7	1047.9	1028.0	1.0557	0.4438
	500.0	13.7	12.9	1094.3	1073.5	1.3611	0.5412

* Test temperature = 35°C

TABLE 5. RESULTS OF DISPLACEMENT TESTS CONDUCTED WITH ALKALINE SOLUTIONS.

Run No.	Displacing Fluid	Temp. (°C)	Oil Recovered (%) at			Tertiary Oil Recovered (%)
			1 PV Water	1 PV Caustic	Final	
1	Distilled Water	25	19.6	22.3	23.7 (2.6 PV)	5.1
4	1 PV water + 2PV 12.5 mM NaOH	25	18.0	46.7	66.1 (3.03 PV)	58.6
13	1 PV water + 2PV 12.5 mM Na ₂ SiO ₃ ·9H ₂ O	25	18.3	51.9	66.1 (3.5 PV)	58.5
7	1 PV water + 2PV 25.0 mM NaOH	25	17.2	48.9	61.1 (2.97 PV)	53.0
16	1 PV water + 2PV 25.0 mM Na ₂ SiO ₃ ·9H ₂ O	25	17.1	38.4	55.4 (3.10 PV)	46.2
10	1 PV water + 2PV 125.0 mM NaOH	25	18.9	48.6	58.5 (3.02 PV)	48.8
19	1 PV water + 2PV 125.0 mM Na ₂ SiO ₃ ·9H ₂ O	25	18.8	42.6	45.6 (2.23 PV)	33.0
2	Distilled Water	45	26.0	28.0	31.2 (3.03 PV)	7.0
5	1 PV water + 2PV 12.5 mM NaOH	45	23.5	33.6	55.5 (2.98 PV)	41.8
14	1 PV water + 2PV 12.5 mM Na ₂ SiO ₃ ·9H ₂ O	45	23.8	33.5	43.5 (3.16 PV)	25.9
8	1 PV water + 2PV 25 mM NaOH	45	21.9	41.0	51.3 (2.99 PV)	37.6
17	1 PV water + 2PV 25 mM Na ₂ SiO ₃ ·9H ₂ O	45	18.9	25.6	30.5 (2.99 PV)	14.3
11	1 PV water + 2PV 125 mM NaOH	45	21.4	35.6	41.7 (2.98 PV)	25.8
20	1 PV water + 2PV 125 mM Na ₂ SiO ₃ ·9H ₂ O	45	22.1	30.4	33.1 (3.02 PV)	14.1
3	Distilled water	65	29.0	33.5	36.5 (2.82 PV)	10.6
6	1 PV water + 2PV 12.5 mM NaOH	65	26.1	33.5	43.8 (2.98 PV)	23.9
15	1 PV water + 2PV 12.5 mM Na ₂ SiO ₃ ·9H ₂ O	65	27.0	33.7	46.7 (3.06 PV)	27.0
9	1 PV water + 2PV 25.0 mM NaOH	65	22.2	34.9	46.5 (3.01 PV)	31.2
18	1 PV water + 2PV 25.0 mM Na ₂ SiO ₃ ·9H ₂ O	65	24.0	31.9	39.1 (3.17 PV)	19.9
12	1 PV water + 2PV 125.0 mM NaOH	65	27.4	31.0	36.5 (2.99 PV)	12.5
21	1 PV water + 2PV 125.0 mM Na ₂ SiO ₃ ·9H ₂ O	65	26.8	29.0	32.7 (3.06 PV)	8.1

TABLE 6: RESULTS OF DISPLACEMENT TESTS CONDUCTED WITH SA FORMULATIONS.

Run No.	Displacing Fluid (1 PV Water +)	Temp. (°C)	Oil Recovered (%) at			Tertiary Oil Recovered (%)
			1 PV Water	1 PV SA	Final	
22	12.5 mM NaOH + 0.1% B-100	25	17.4	41.4	49.0 (3.0 PV)	38.2
25	25.0 mM NaOH + 0.1% B-100	25	18.5	39.0	41.5 (2.99 PV)	28.2
28	125.0 mM NaOH + 0.1% B-100	25	16.1	39.0	40.5 (3.04 PV)	29.1
23	12.5 mM NaOH + 0.1% B-100	45	20.1	35.5	41.4 (2.99 PV)	26.6
26	25.0 mM NaOH + 0.1% B-100	45	21.6	33.0	37.3 (3.04 PV)	20.0
29	125.0 mM NaOH + 0.1% B-100	45	22.5	48.3	50.2 (3.00 PV)	35.7
24	12.5 mM NaOH + 0.1% B-100	65	24.9	31.6	36.5 (2.99 PV)	15.4
27	25.0 mM NaOH + 0.1% B-100	65	34.1	39.7	44.8 (3.01 PV)	16.2
30	125.0 mM NaOH + 0.1% B-100	65	32.2	38.3	40.9 (2.98 PV)	12.8

TABLE 7. RESULTS OF DISPLACEMENT TESTS CONDUCTED WITH POLYMER AND PSA SYSTEMS.

Run No.	Displacing Fluid 1 PV Water +	Viscosity 6 rpm	TEMP °C	Oil Recovered (%) at				Tertiary Oil Recovered (%)	μ_o/μ_w
				1 PV Water	1 PV PSA	Final			
32	0.5% Polyox	155	25	17.6	51.9	65.7 (2.77 PV)		58.4	3.1
35	12.5 mM NaOH + 0.1% B-100 + 0.5% Polyox	145	25	17.6	68.0	84.1 (2.66 PV)		80.7	3.3
38	250 mM NaOH + 0.1% B-100 + 0.5% Polyox	130	25	17.0	70.4	84.8 (2.57 PV)		81.7	3.6
51	125 mM NaOH + 0.1% B-100 + 0.5% Polyox	120	25	19.2	69.0	76.0 (2.38 PV)		70.3	3.9
33	0.5 polyox	85	45						
36	125 mM NaOH + 0.1% B-100 + 0.5% Polyox	70	45	16.1	58.9	77.3 (2.89 PV)		72.9	1.5
39	250 mM NaOH + 0.1% B-100 + 0.5% Polyox	70	45	21.6	65.0	78.4 (2.98 PV)		72.4	1.9
42	125 mM NaOH + 0.1% B-100 + 0.5% Polyox	55	45	24.5	66.9	76.0 (2.52 PV)		68.2	1.9
34	0.5% Polyox	40	65	22.4	69.8	89.9 (2.59 PV)		87.0	2.4
37	125 mM NaOH + 0.1% B-100 + 0.5% Polyox	30	65	28.1	58.5	79.7 (2.93 PV)		71.8	1.1
40	25.0 mM NaOH + 0.1% B-100 + 0.5% Polyox	30	65	24.4	63.5	78.5 (2.88 PV)		71.6	1.5
43	125 mM NaOH + 0.1% B-100 + 0.5% Polyox	27	65	22.3	70.0	83.7 (2.62 PV)		79.0	1.5
45	0.5% SP ² PAM	40	25	18.1	50.0	57.9 (2.83 PV)		48.6	10.5
48	12.5 mM NaOH + 0.1% B-100 + PAM	340	25	17.3	65.1	78.2 (2.51 PV)		73.6	1.4
51	25.0 mM NaOH + 0.1% B-100 + PAM	500	25	18.5	62.9	81.9 (2.58 PV)		77.8	0.9
54	125 mM NaOH + 0.1% B-100 + PAM	215	25	14.0	64.2	79.7 (2.36 PV)		76.4	2.2
46	0.5% SP ² PAM	28	45	20.6	62.1	71.8 (2.87 PV)		64.5	4.6
49	12.5 mM NaOH + 0.1% B-100 + PAM	265	45	20.2	66.6	89.3 (2.52 PV)		86.6	0.5
52	25.0 mM NaOH + 0.1% B-100 + PAM	400	45	18.4	66.0	83.4 (2.49 PV)		79.7	0.3
55	125.0 mM NaOH + 0.1% B-100 + PAM	150	45	20.6	60.0	76.6 (2.58 PV)		70.5	0.9
47	0.5% SP ² PAM	25	65	26.2	55.0	60.1 (2.89 PV)		45.9	1.8
50	12.5 mM NaOH + 0.1% B-100 + PAM	200	65	24.5	70.0	76.4 (2.34 PV)		68.7	0.2
53	25.0 mM NaOH + 0.1% B-100 + PAM	350	65	25.7	63.0	80.9 (2.53 PV)		74.3	0.1
56	125.0 mM NaOH + 0.1% B-100 + PAM	130	65	25.1	72.5	89.7 (2.44 PV)		86.2	0.3

TABLE 8: FINAL EQUILIBRIUM IFT MODEL PARAMETER ESTIMATES

Temp (°C)	$K_{D_{HA}}$ (moles/L)	K_s (moles/L)	n_{CH_2}
25	8.0×10^{-10}	1.28×10^{-4}	13.0
35	5.74×10^{-9}	1.11×10^{-4}	13.4
45	6.89×10^{-8}	1.56×10^{-4}	13.2
55	9.16×10^{-8}	3.19×10^{-4}	13.0
65	8.47×10^{-8}	1.45×10^{-4}	14.0
75	4.75×10^{-8}	1.10×10^{-4}	13.7

TABLE 9: TEMPERATURE CORRELATION COEFFICIENTS FOR $K_{D_{HA}}$

Coefficient	Estimate	Standard Error
β_0	169	28
β_1	-1.08×10^5	0.18×10^5
β_2	1.8×10^7	0.29×10^7

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- 15 IFT versus Time for 125 mM NaOH+ Additives Against Court Crude at 65°C

16	IFT versus Time for Binary SA Systems (25 mM NaOH+ Additives) Against Court Crude at 25°C
17	IFT versus Time for Binary SA Systems (25 mM NaOH+ Additives) Against Court Crude at 65°C
18	IFT versus Time for Binary SA Systems (125 mM NaOH+ Additives) Against Court Crude at 25°C
19	IFT versus Time for Ternary PSA Systems (12.5 mM NaOH+ Additives) Against Court Crude at 25°C
20	IFT versus Time for Ternary PSA Systems (12.5 mM NaOH+ Additives) Against Court Crude at 45°C
21	IFT versus Time for Ternary PSA Systems (25.0 mM NaOH+ Additives) Against Court Crude at 25°C
22	IFT versus Time for Ternary PSA Systems (125.0 mM NaOH+ Additives) Against Court Crude at 25°C
23	IFT versus Time for Ternary PSA Systems (125.0 mM NaOH+ Additives) Against Court Crude at 65°C
24	Effect of Age on the Viscosity of NaOH/SP ² PAM Systems
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26	Oil Recovery Histories for Water and NaOH Displacing Court Crude at 25° C . . .
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32	Relative Permeability Versus Saturation for 12.5 mM NaOH and 25° C . .
33	Fractional Flow of Water Versus Saturation for 12.5 mM NaOH and 25° C
A1	Variation of Actual and Predicted K_{HA}^D with 1/T
A2	Residuals Versus 1/T

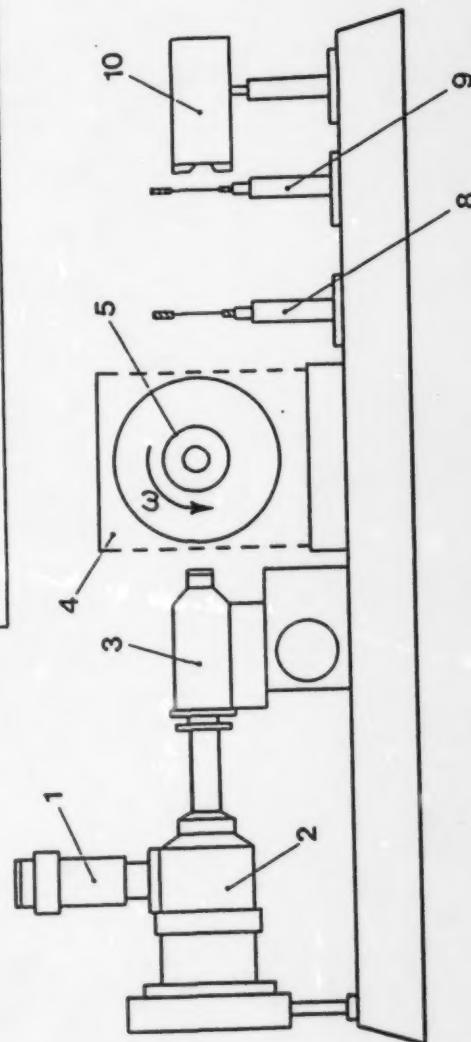
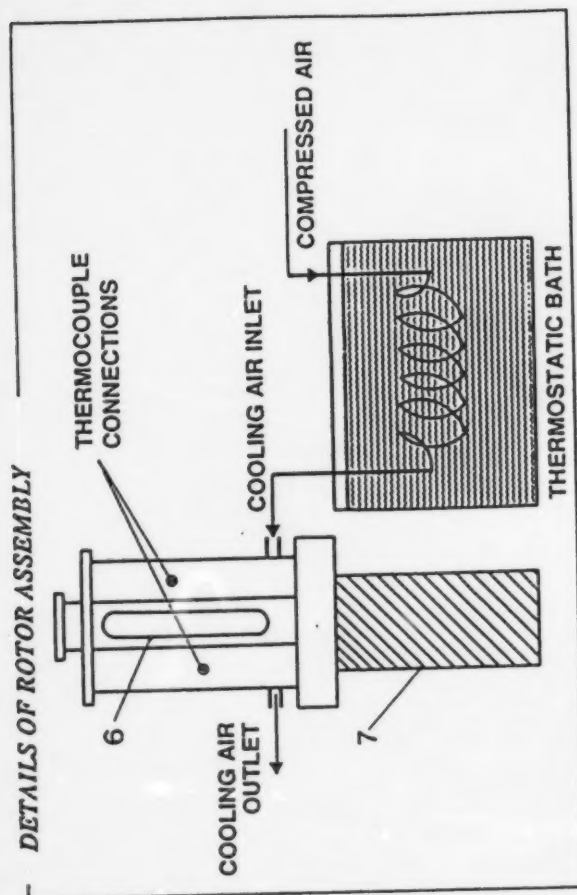


Fig. 1 : Elements of the Modified Spinning Drop Photo-Tensiometer

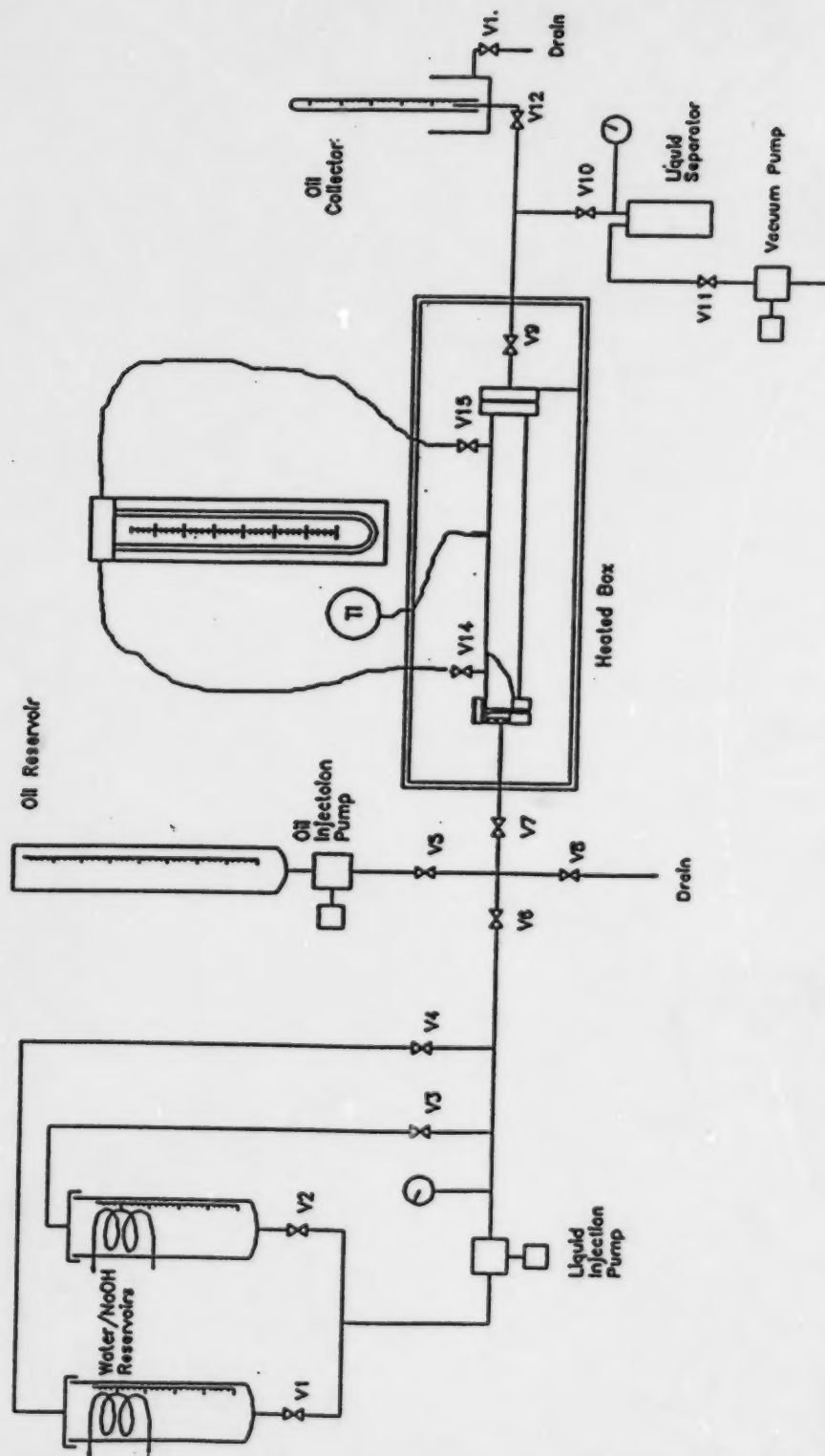


Fig. 2 : Schematic of the Oil Displacement System

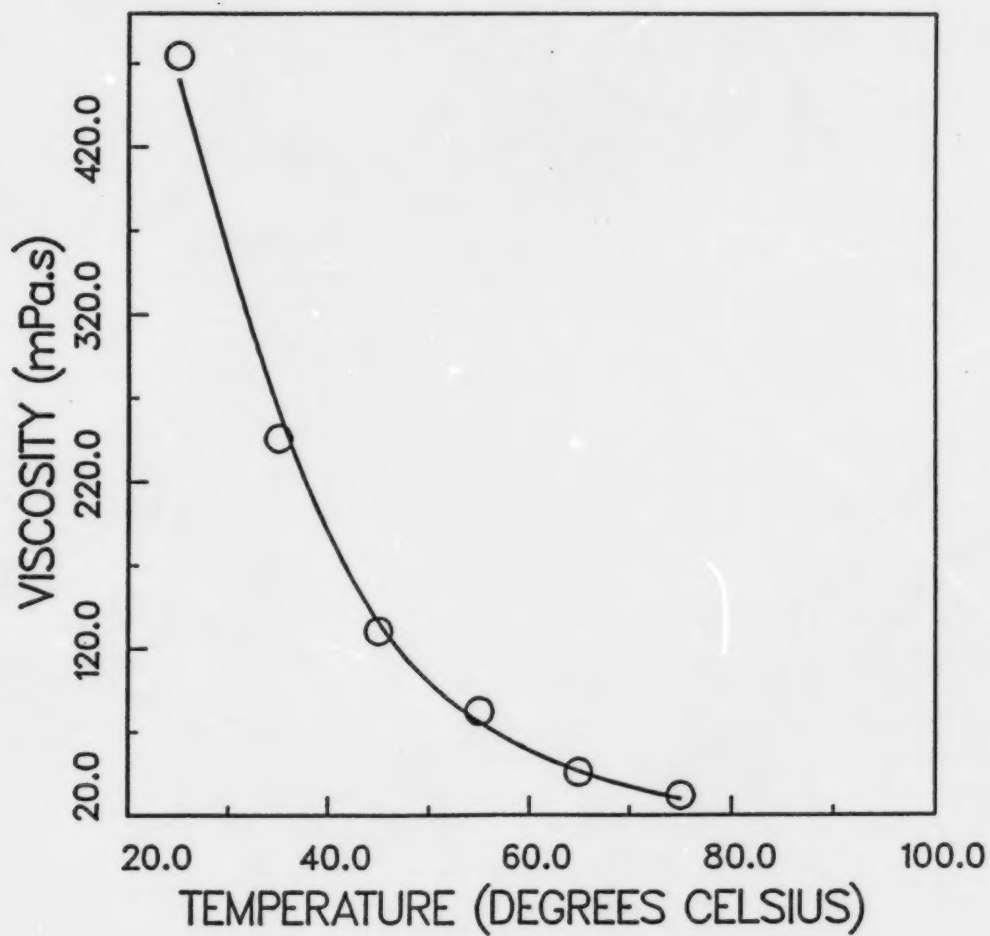


Fig. 3: Effect of Temperature on the Viscosity of Court Crude

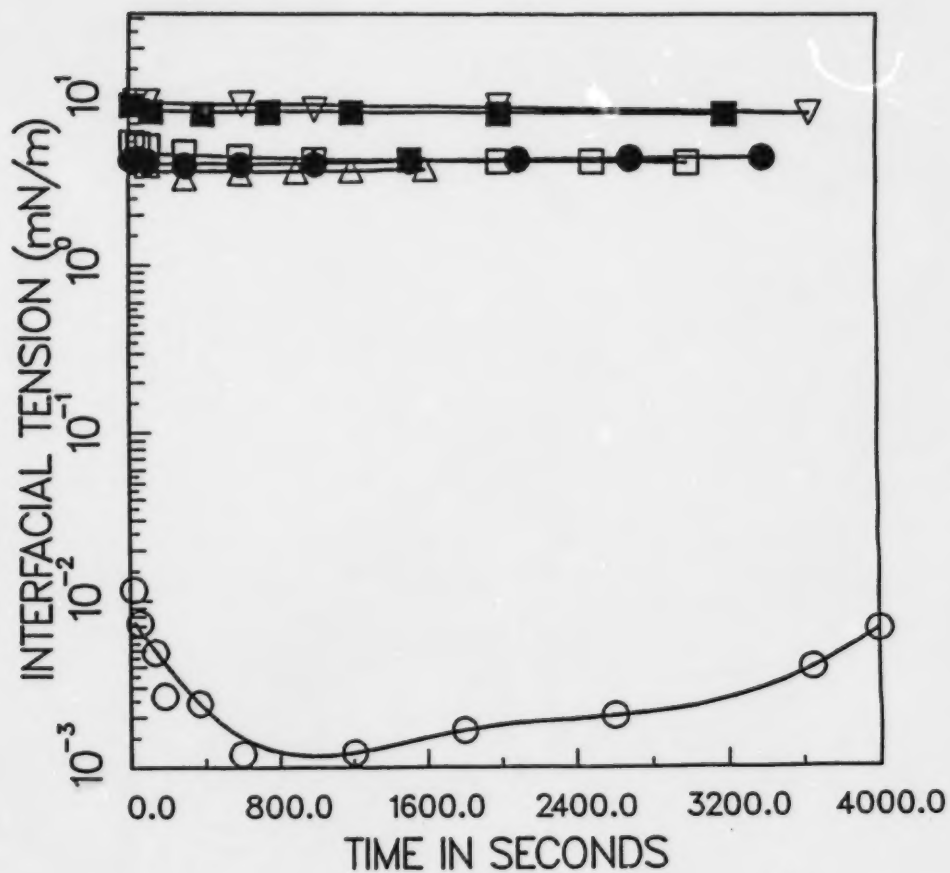


Fig. 4: Dynamic IFT Behaviour of Court Crude against 1.25 mM NaOH, Na₂SiO₃ and Na₄SiO₄ at 25°C and 65°C: (Δ — Δ , NaOH at 25°C; ∇ — ∇ , NaOH at 65°C; $\square$ — $\square$, Na₂SiO₃ at 25°C, $\blacksquare$ — $\blacksquare$, Na₂SiO₃ at 65°C; $\circ$ — $\circ$, Na₄SiO₄ at 25°C; $\bullet$ — $\bullet$, Na₄SiO₄ at 65°C)

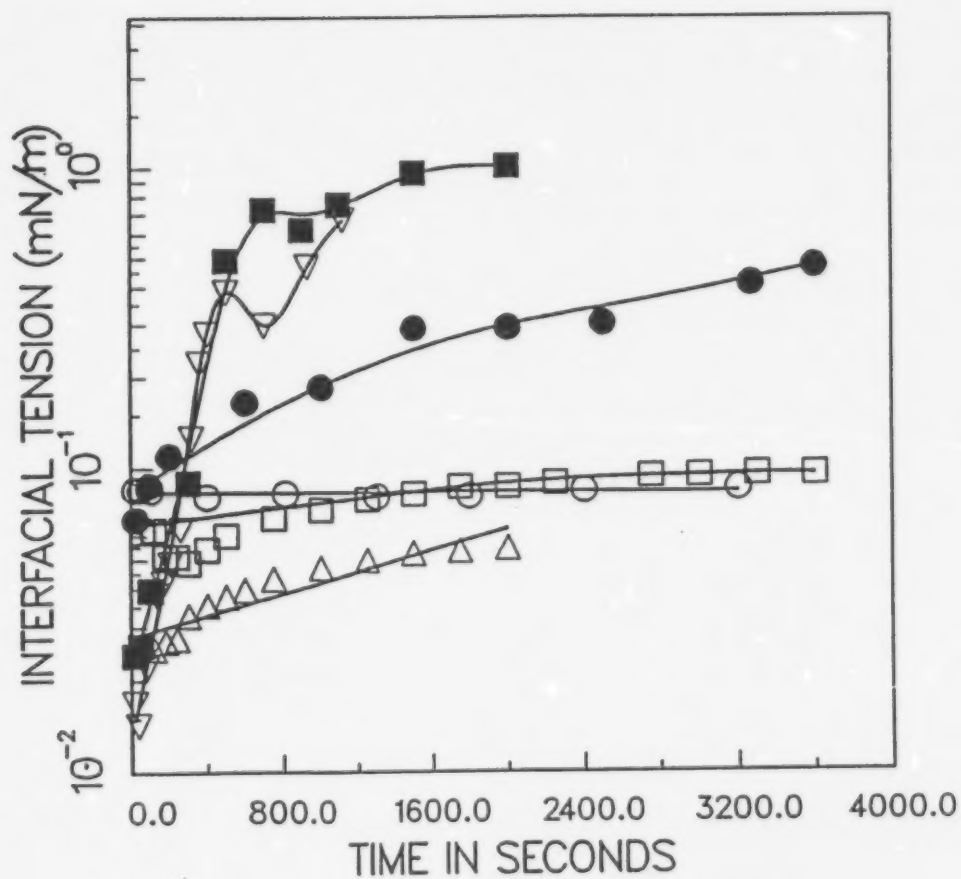


Fig. 5 : Dynamic IFT Behaviour of Court Crude against 25.0 mM NaOH, Na_2SiO_3 and Na_4SiO_4 at 25°C and 65°C: ($\triangle$ — $\triangle$, NaOH at 25°C; ∇ — ∇ , NaOH at 65°C; $\square$ — $\square$, Na_2SiO_3 at 25°C; $\blacksquare$ — $\blacksquare$, Na_2SiO_3 at 65°C; $\circ$ — $\circ$, Na_4SiO_4 at 25°C; $\bullet$ — $\bullet$, Na_4SiO_4 at 65°C)

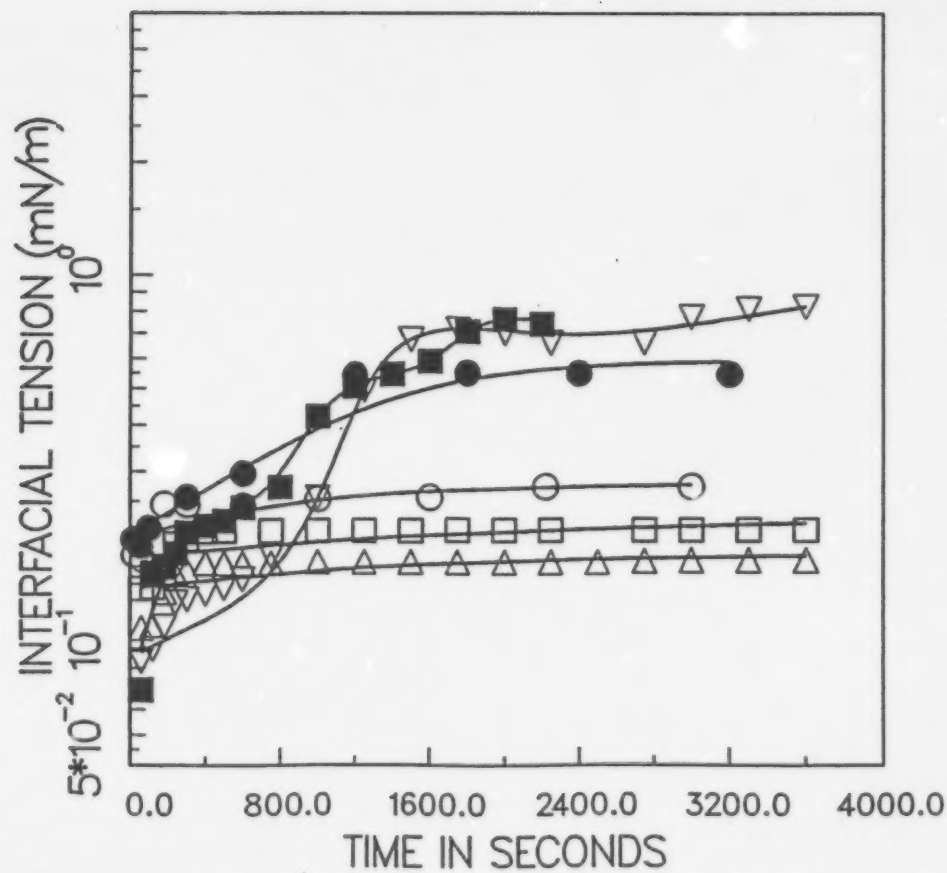


Fig. 6 : Dynamic IFT Behaviour of Court Crude against 125 mM NaOH, Na_2SiO_3 and Na_4SiO_4 at 25°C and 65°C: ($\triangle$ — $\triangle$, NaOH at 25°C; ∇ — ∇ , NaOH at 65°C; $\square$ — $\square$, Na_2SiO_3 at 25°C; $\blacksquare$ — $\blacksquare$, Na_2SiO_3 at 65°C; $\circ$ — $\circ$, Na_4SiO_4 at 25°C; $\bullet$ — $\bullet$, Na_4SiO_4 at 65°C)

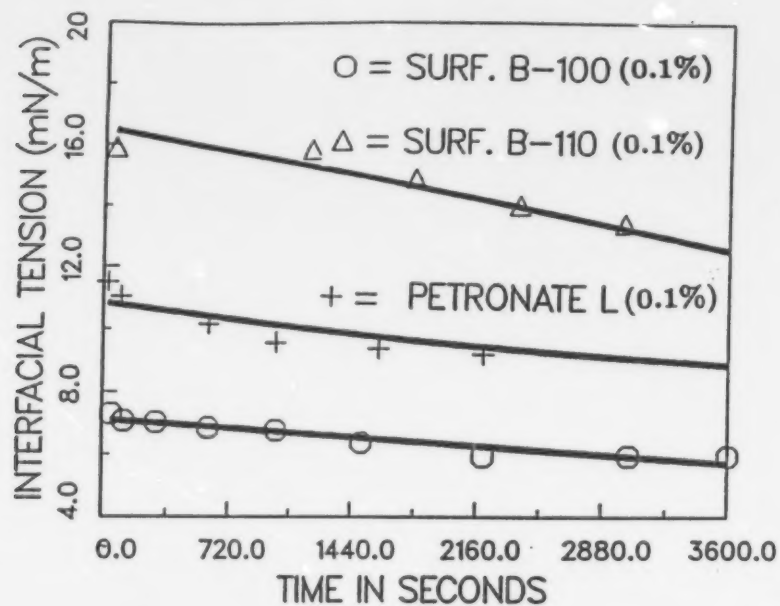


Fig. 7 : IFT VERSUS TIME FOR VARIOUS SURFACTANTS
WITH COURT CRUDE, TEMP= 25°C

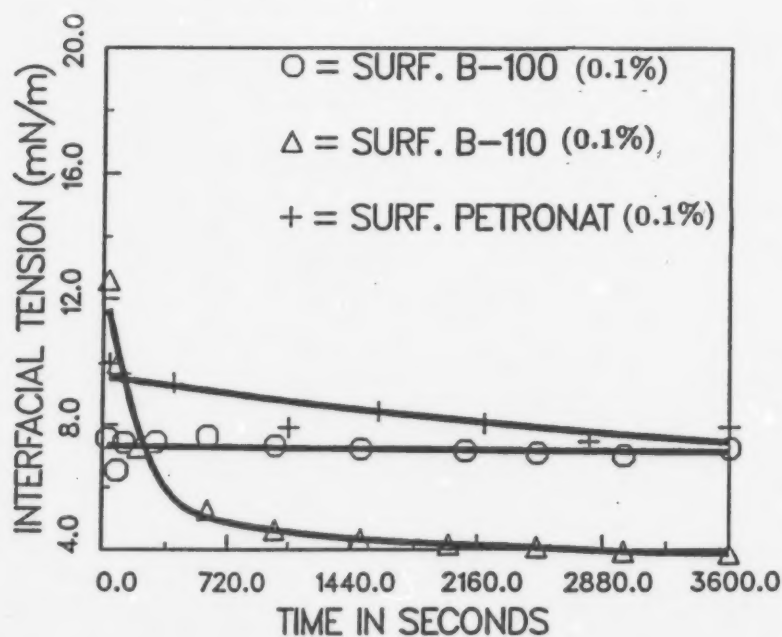


Fig. 8 : IFT VERSUS TIME FOR VARIOUS SURFACTANTS
WITH COURT CRUDE, TEMP= 65°C

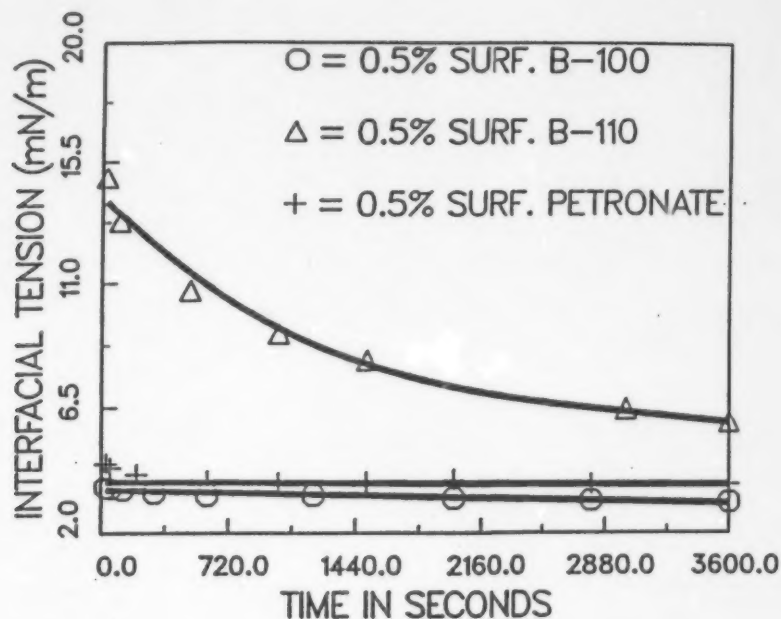


Fig. 9 : IFT VERSUS TIME FOR VARIOUS SURFACTANTS
WITH COURT CRUDE, TEMP= 25°C

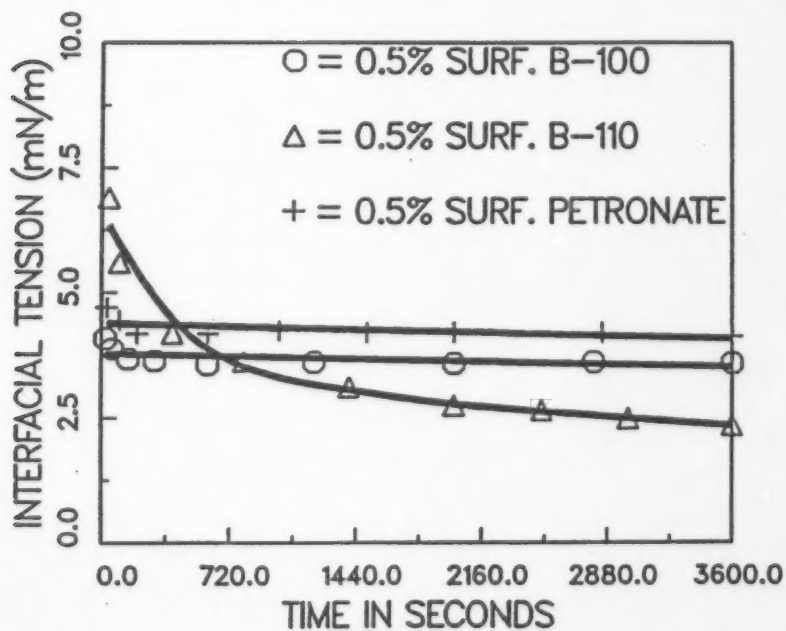


Fig. 10 : IFT VERSUS TIME FOR VARIOUS SURFACTANTS
WITH COURT CRUDE, TEMP= 65°C

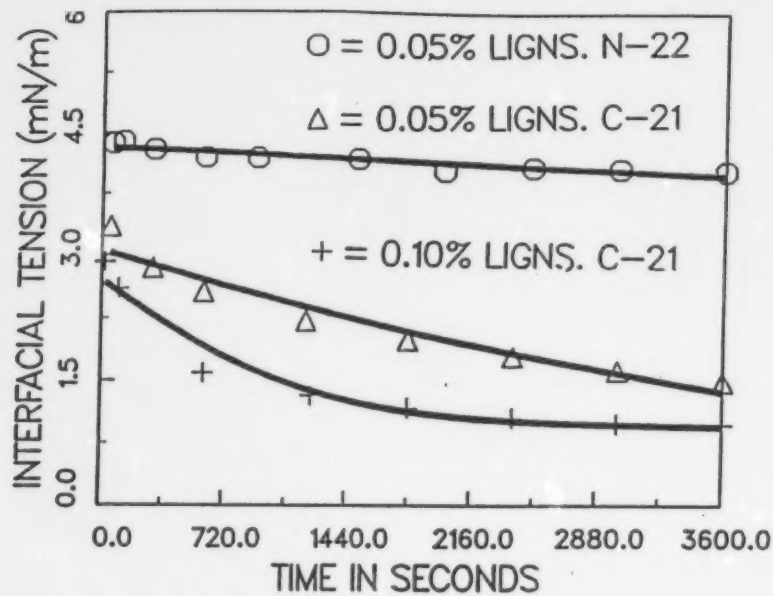


Fig. 11 : IFT VERSUS TIME FOR 0.1% B-100+LIGNS. C-21/ N-22
WITH COURT CRUDE, TEMP= 25°C

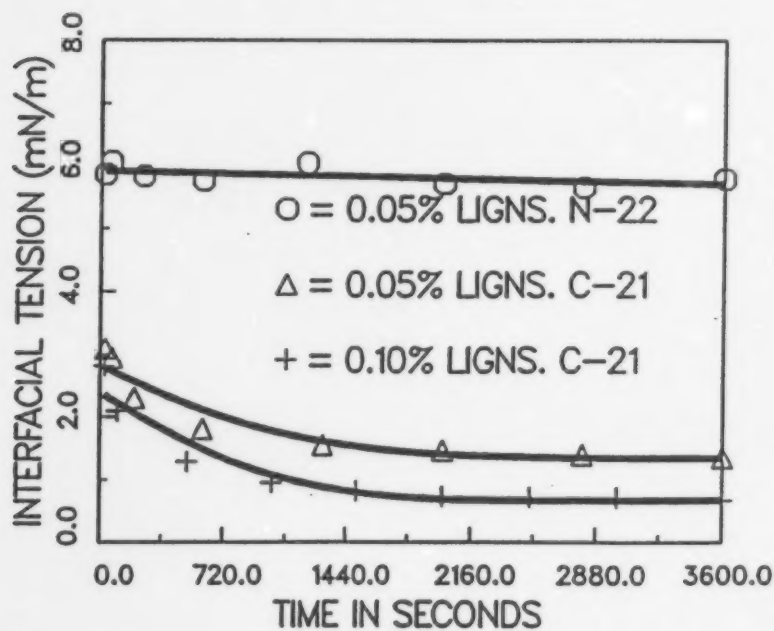


Fig. 12 : IFT VERSUS TIME FOR 0.1% B-100+LIGNS. C-21/ N-22
WITH COURT CRUDE, TEMP= 65°C

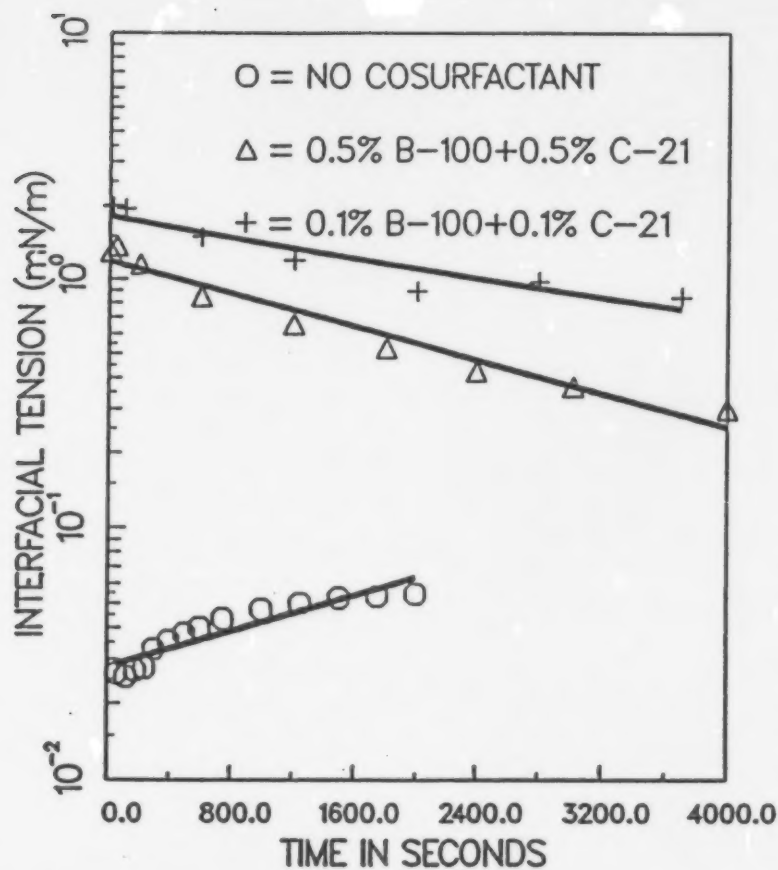


Fig. 13 : IFT VERSUS TIME FOR 25 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C

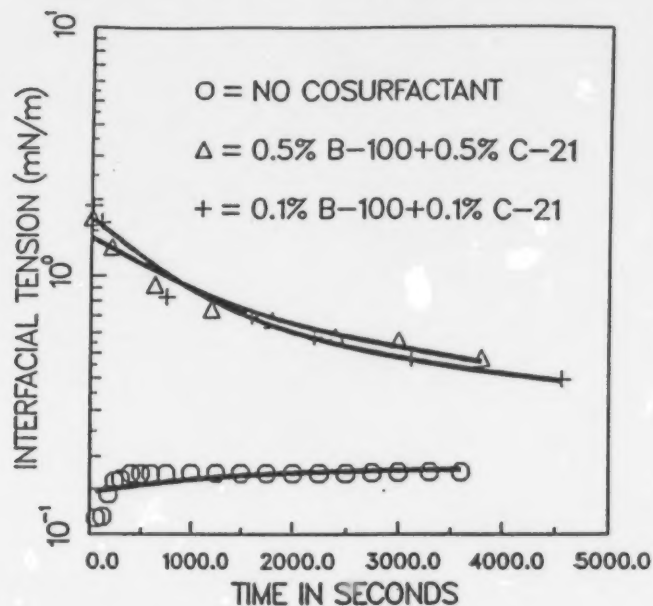


Fig. 14 : IFT VERSUS TIME FOR 125 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C

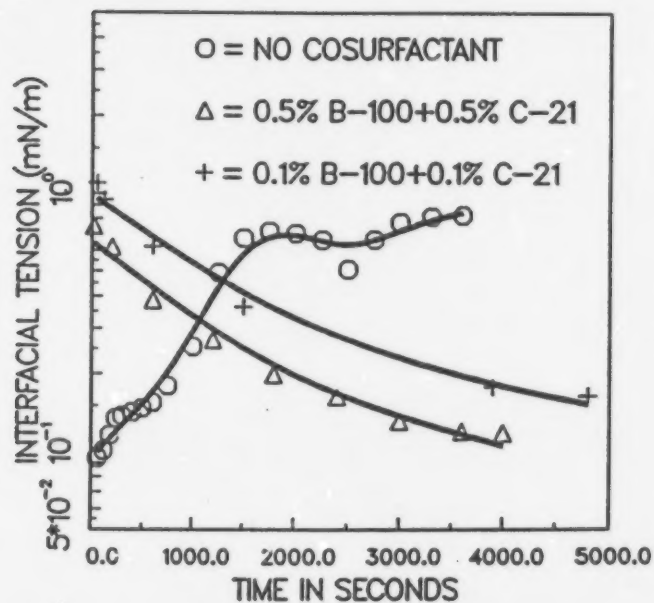


Fig. 15 : IFT VERSUS TIME FOR 125 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 65°C

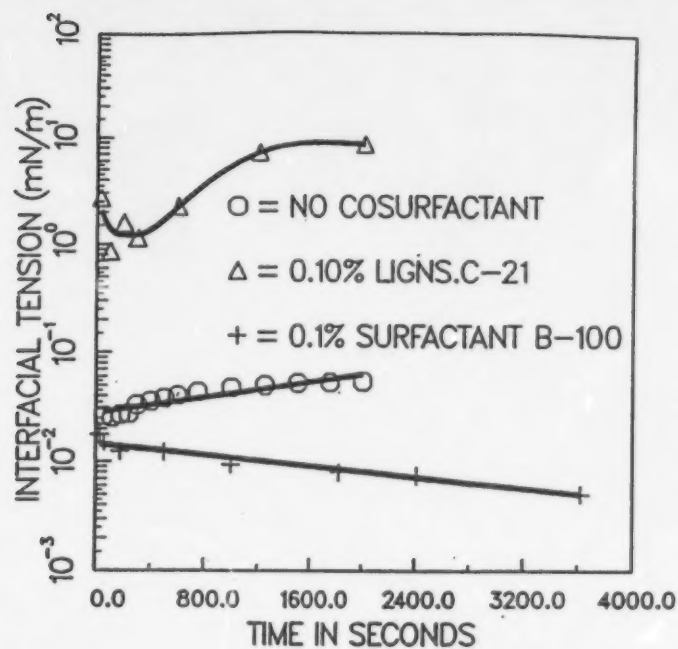


Fig. 16 : IFT VERSUS TIME FOR 25 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C

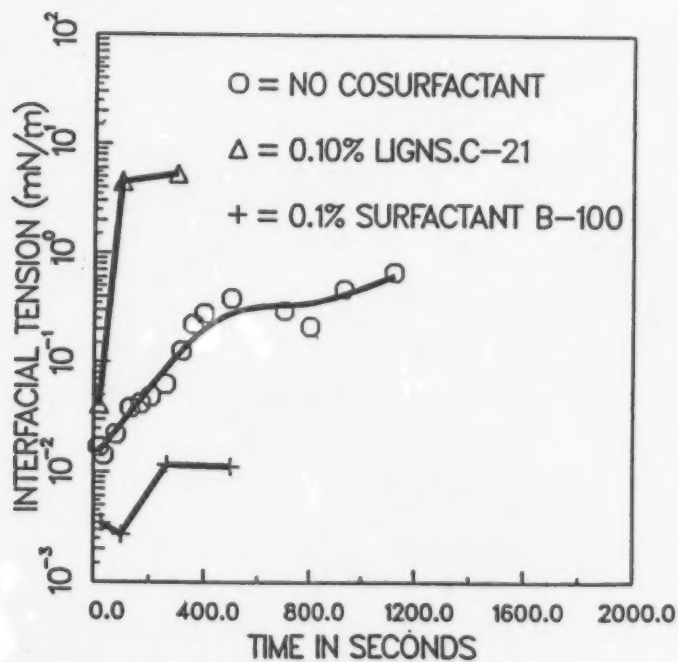


Fig. 17 : IFT VERSUS TIME FOR 25 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 65°C

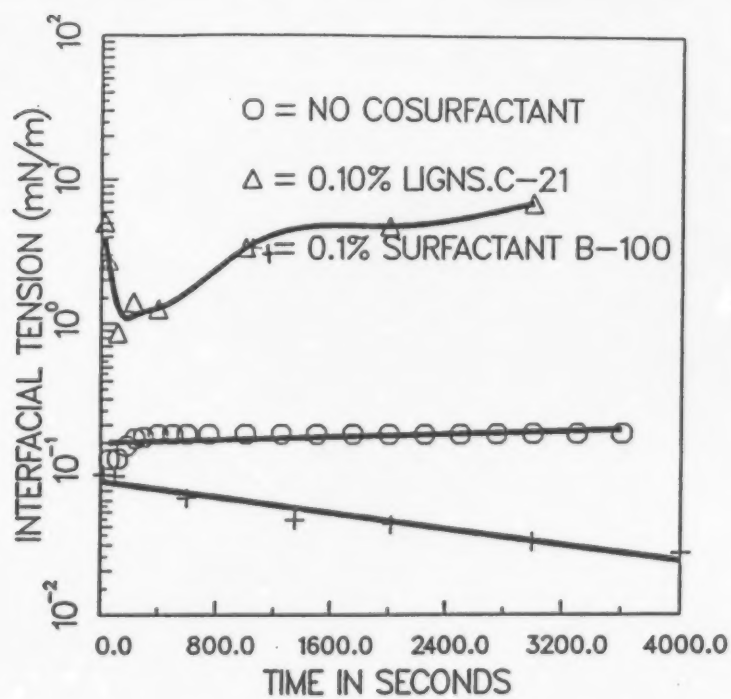


Fig. 18 : IFT VERSUS TIME FOR 125 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C

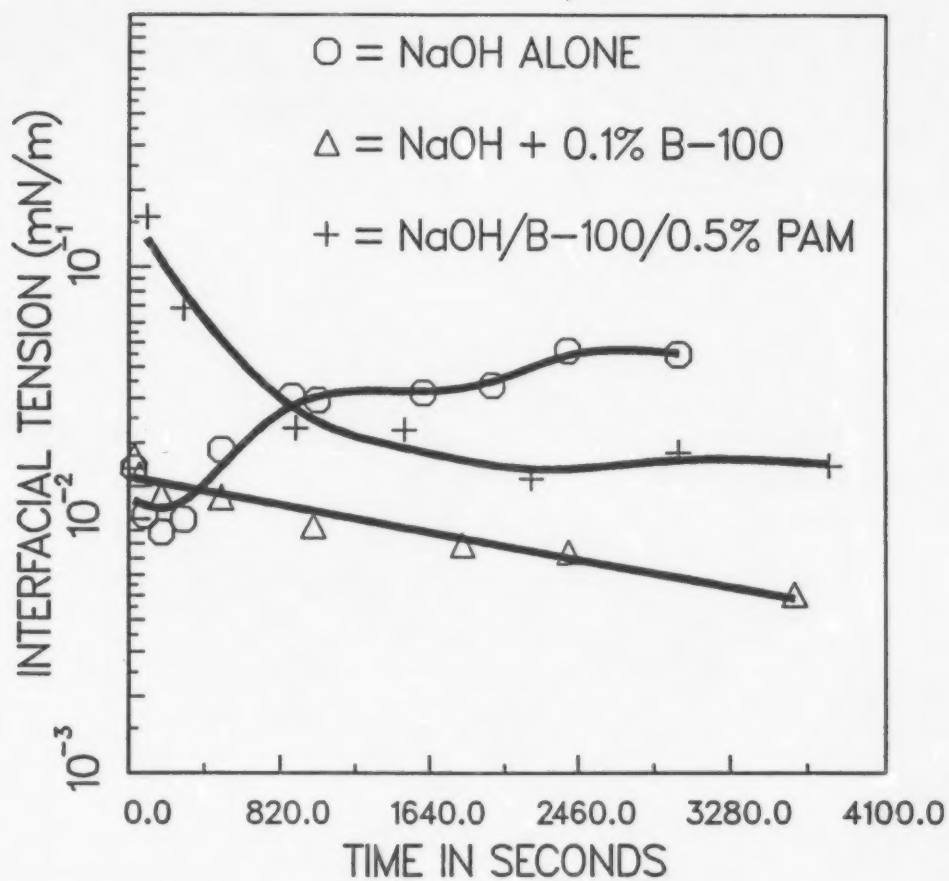


Fig. 19 : IFT VERSUS TIME FOR 12.50 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C, AGE= 7 DAYS

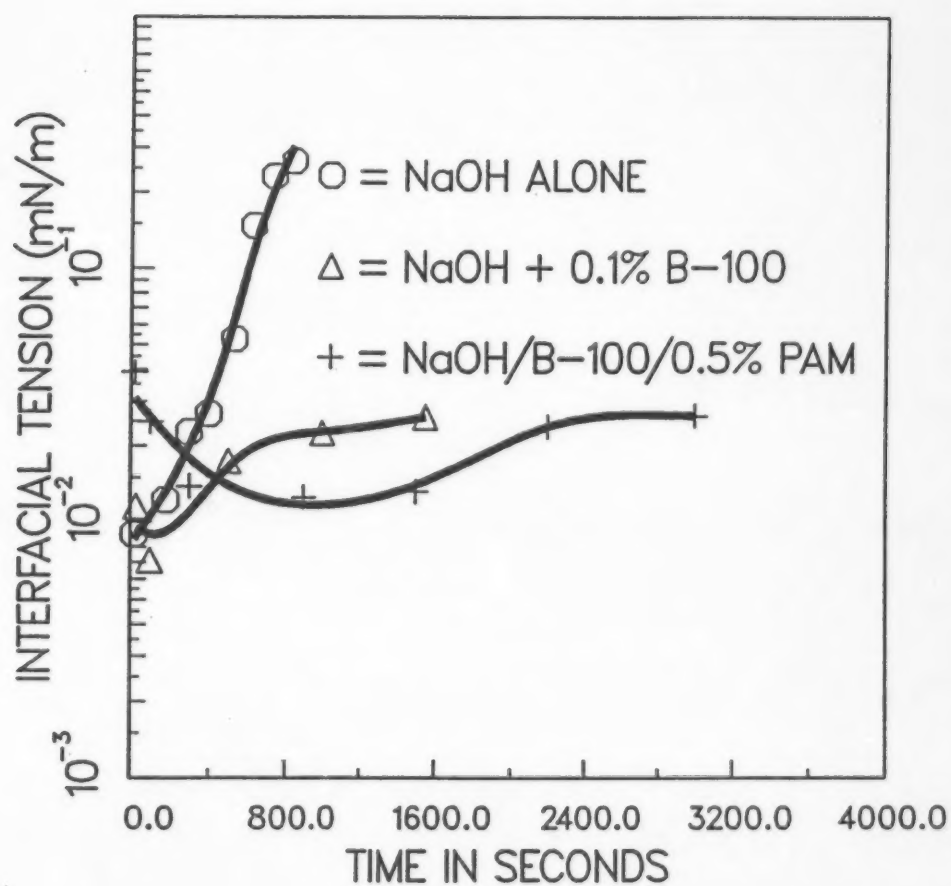


Fig. 20 : IFT VERSUS TIME FOR 12.50 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 45°C, AGE= 7 DAYS

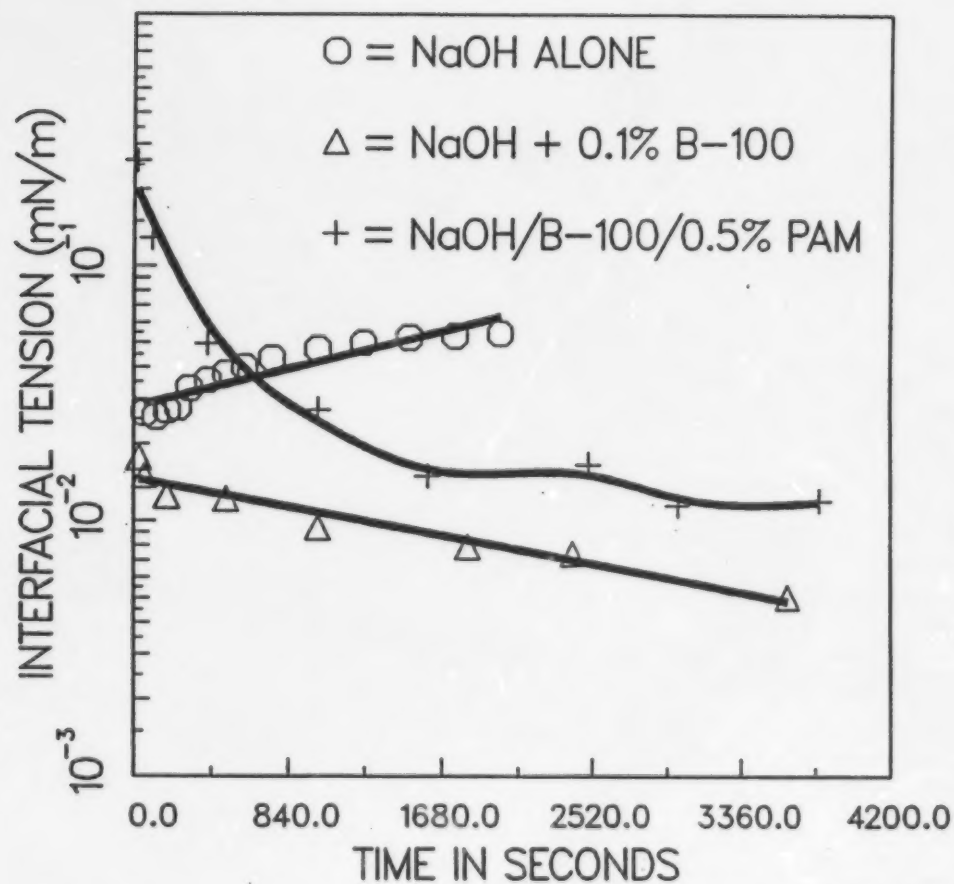


Fig. 21 : IFT VERSUS TIME FOR 25 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C, AGE= 7 DAYS

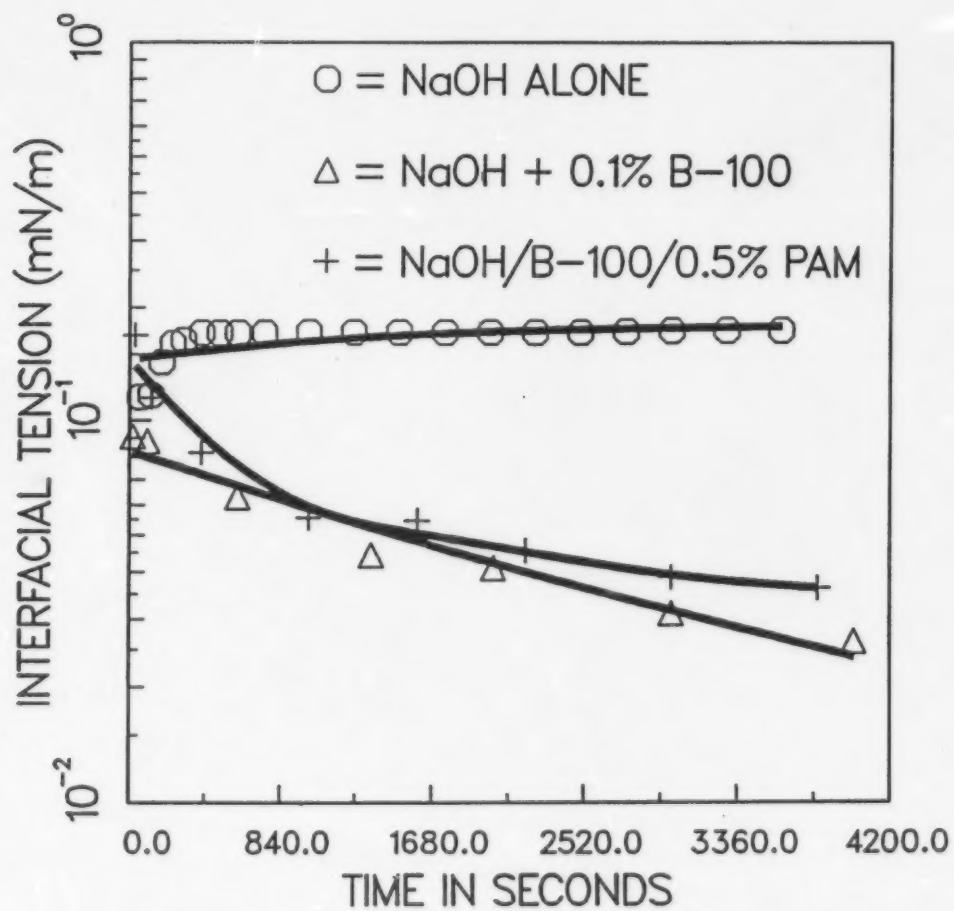


Fig. 22 : IFT VERSUS TIME FOR 125mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 25°C, AGE= 7 DAYS

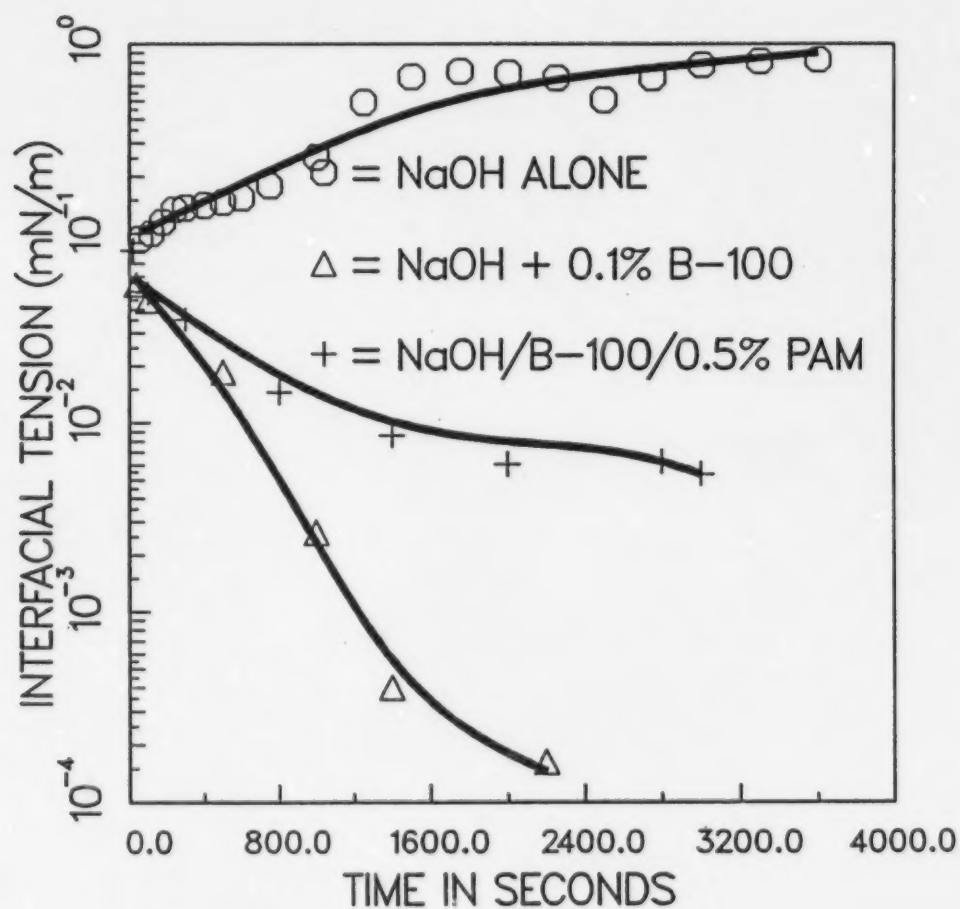


Fig. 23 : IFT VERSUS TIME FOR 125 mM NaOH+ ADDITIVES
WITH COURT CRUDE, TEMP= 65°C, AGE= 7 DAYS

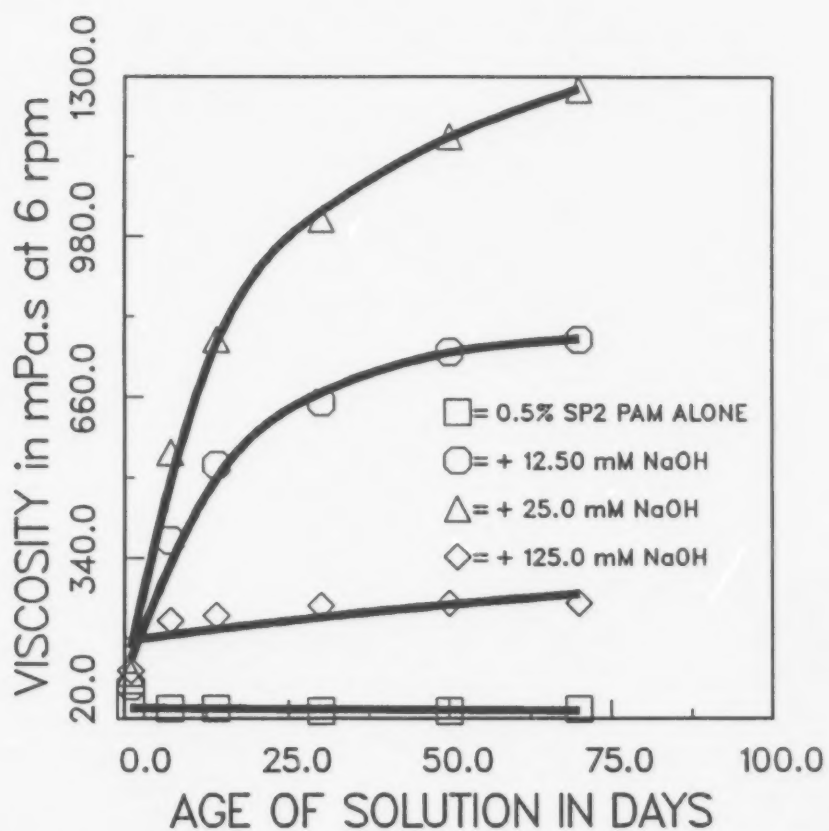


Fig. 24 : Effect of Age on the Viscosity of NaOH-SP² PAM Systems

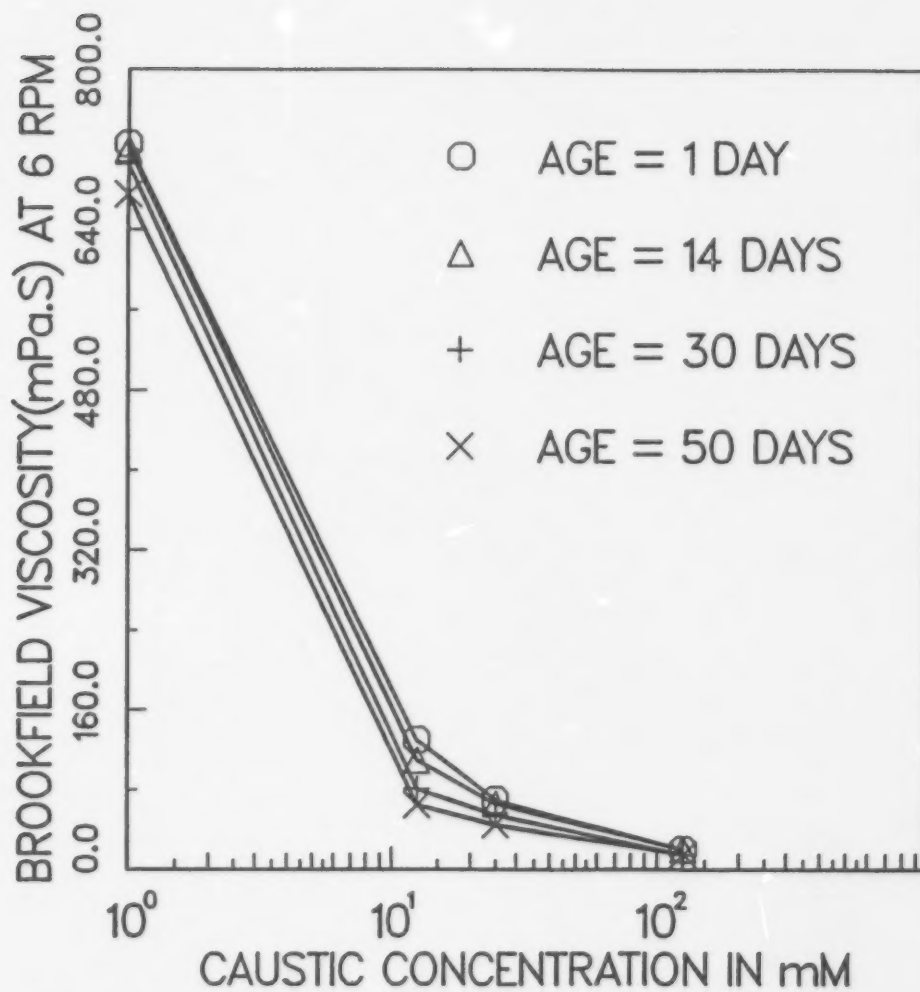


Fig. 25 : Effect of Age on the Viscosity of NaOH/Calgon R-300 Systems

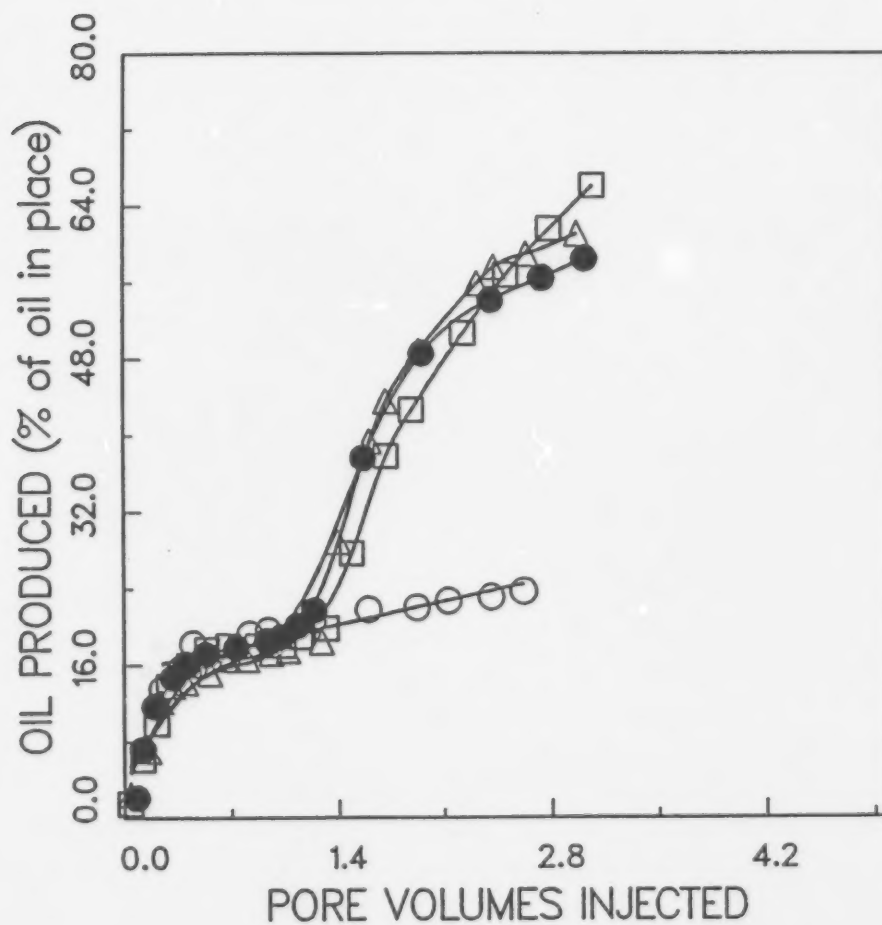


Fig. 26 : Oil Recovery Histories for Water and NaOH Displacing Court Crude at 25°C
 (○—○, Water; □—□, 12.5 mM NaOH; △—△, 25.0 mM NaOH;
 ●—●, 125 mM NaOH)

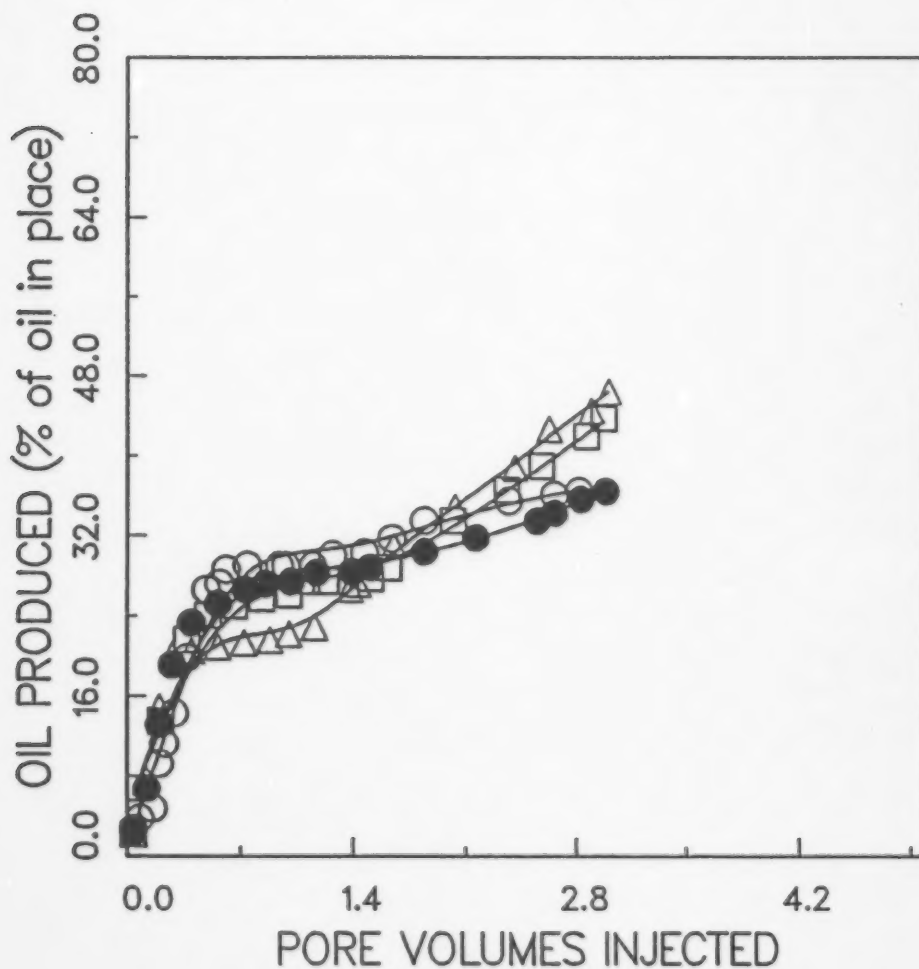


Fig. 27 : Oil Recovery Histories for Water and NaOH Displacing Court Crude at 65°C
 (○—○, Water; □—□, 12.5 mM NaOH; △—△, 25.0 mM NaOH;
 ●—●, 125 mM NaOH)

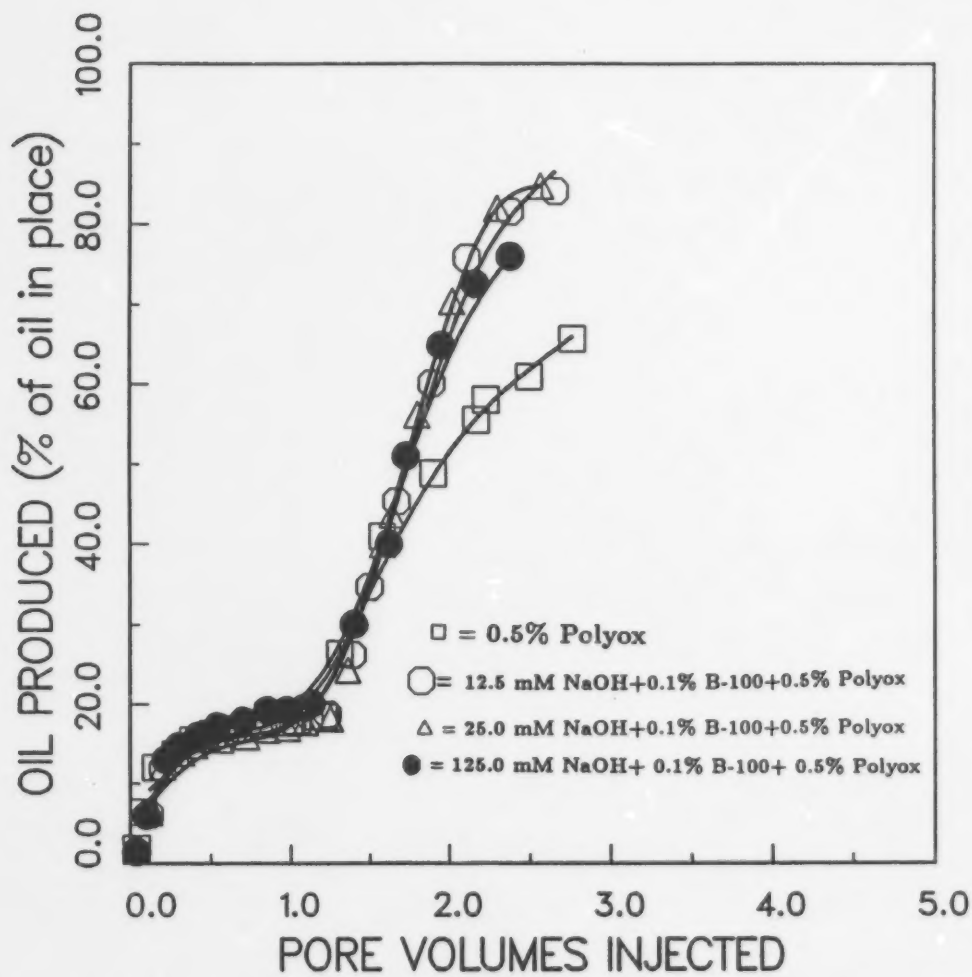


Fig. 28 : Production History for 0.5% Polyox and Polyox-Caustic Systems at 25°C

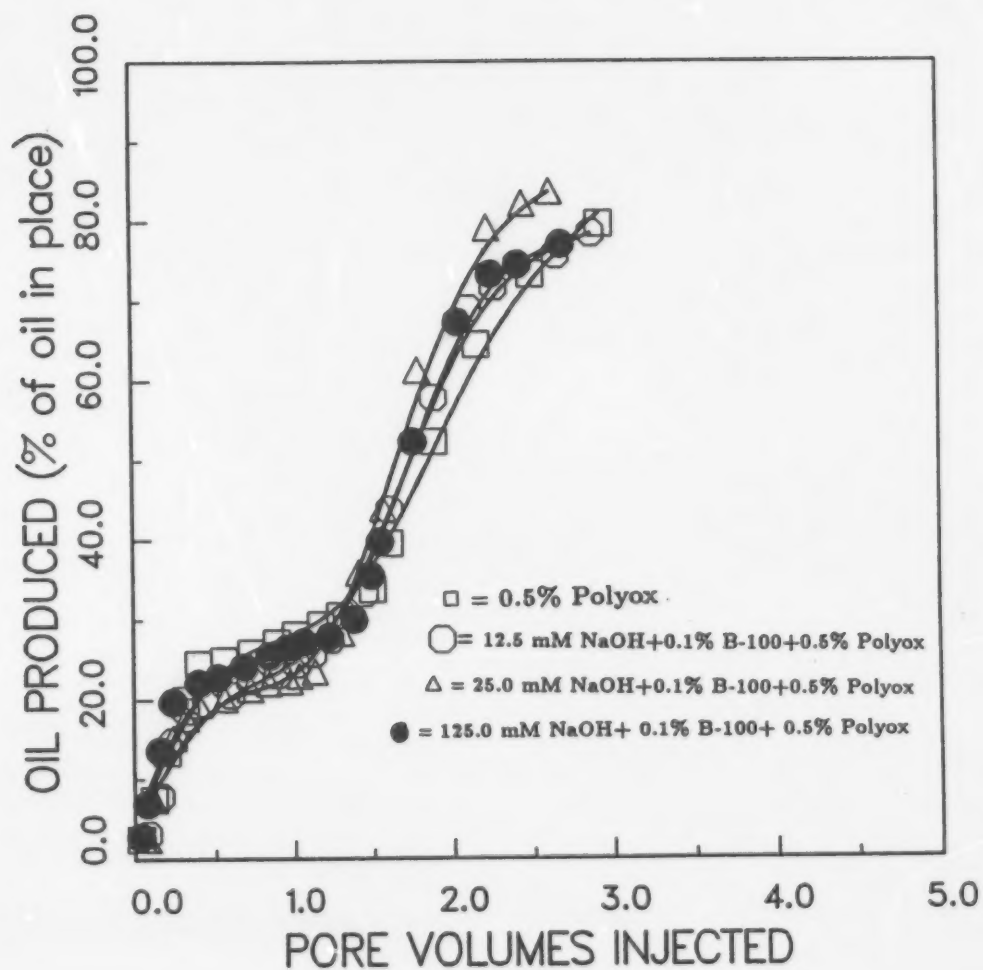


Fig. 29 : Production History for 0.5% Polyox and Polyox-Caustic Systems at 65°C

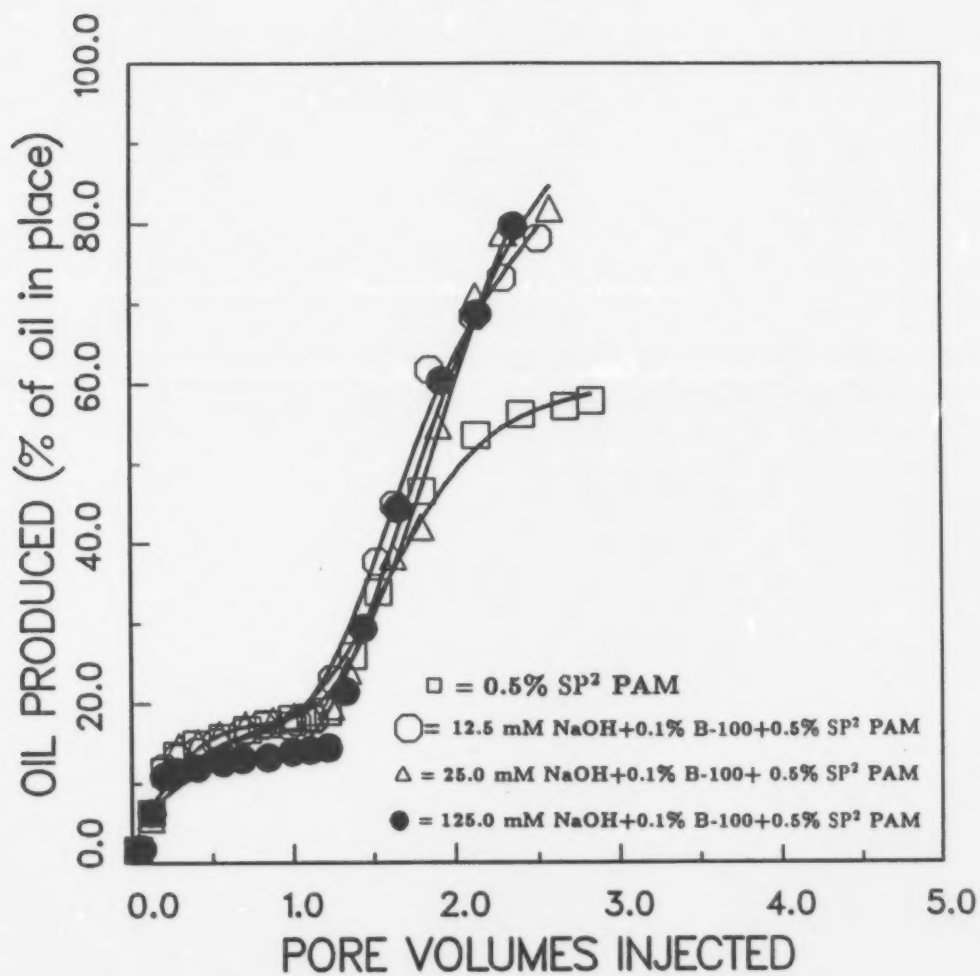


Fig. 30 : Production History for 0.5% SP² and SP²-Caustic Systems at 25°C

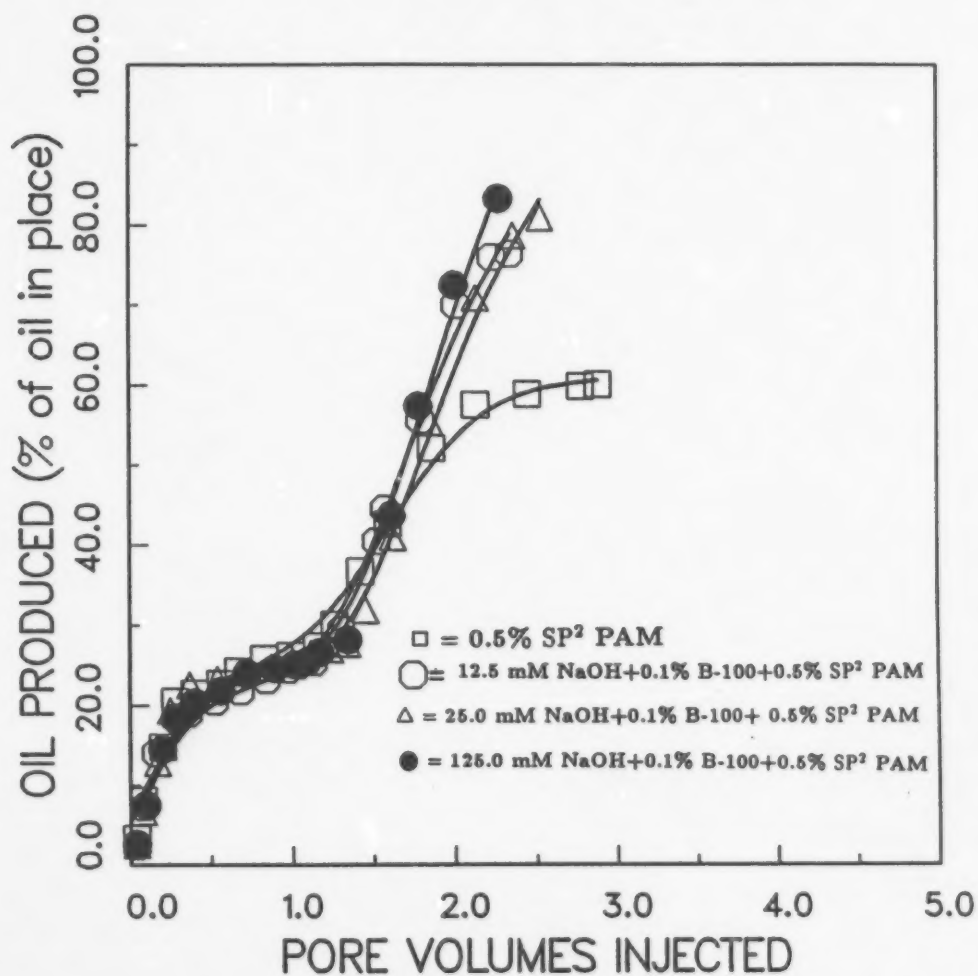


Fig. 31 : Production History for 0.5% SP² and SP²-Caustic Systems at 65°C

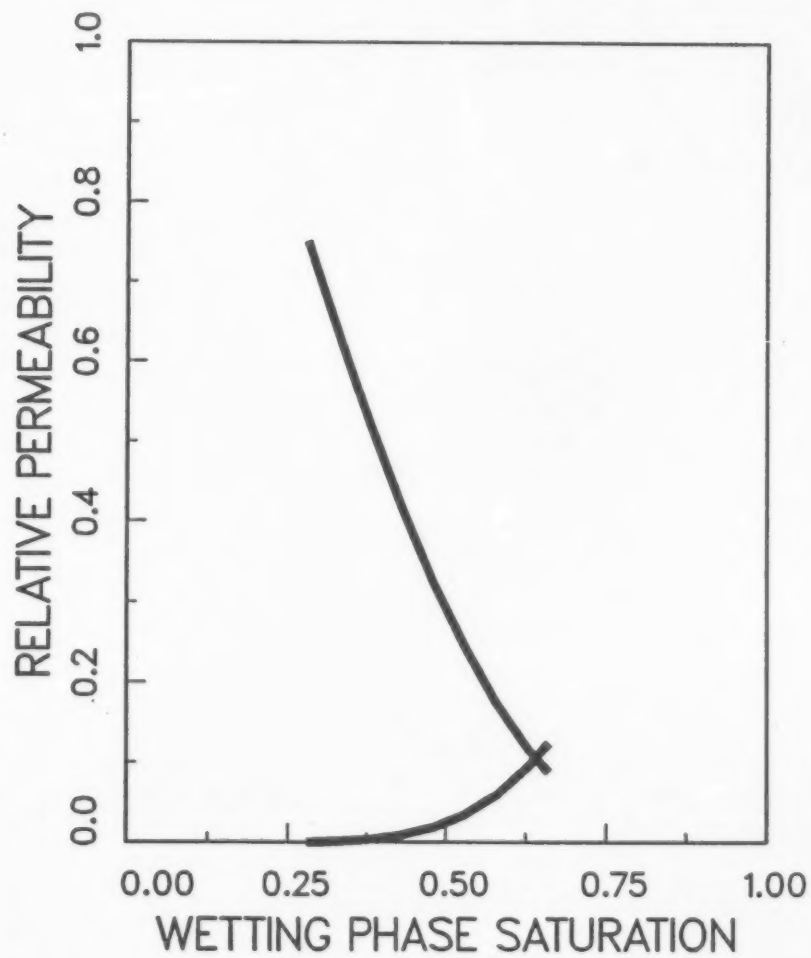


Fig. 32 : Relative Permeability Versus Saturation for 12.5 mM NaOH and 25°C

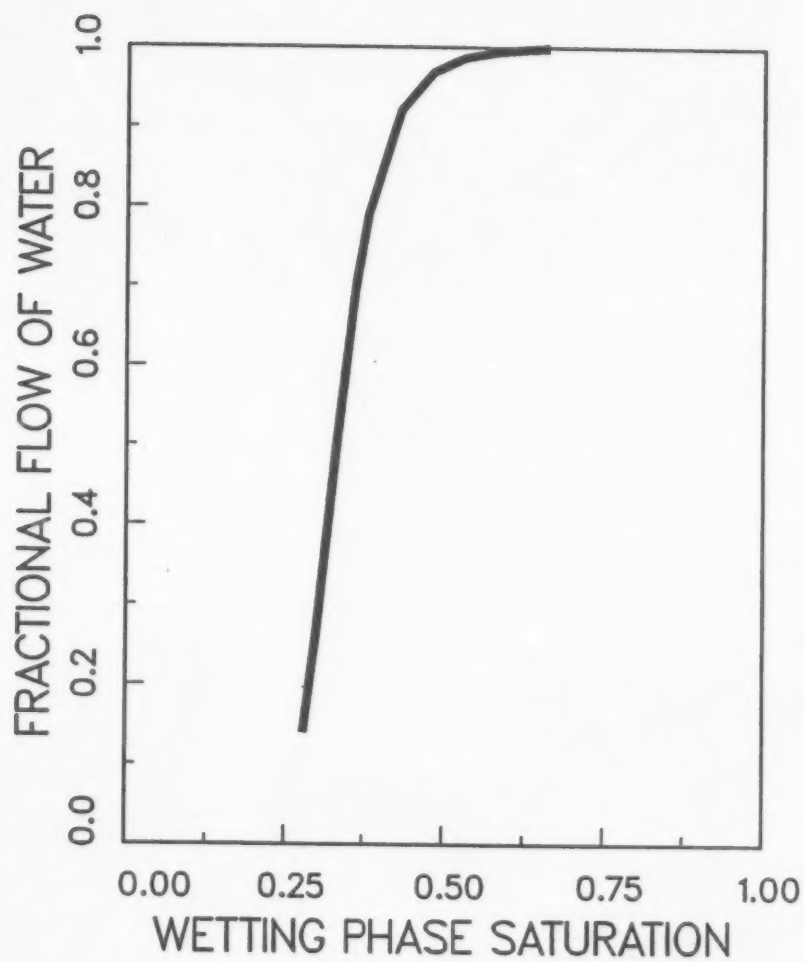


Fig. 33 : Fractional Flow of Water Versus Saturation for 12.5 mM NaOH and 25°C

APPENDIX

Equilibrium IFT Data and Residual Plots

Table A1: EQUILIBRIUM IFT DATA FOR NaOH / COURT CRUDE AT 25°C

NaOH Conc (mM)	Oil-Water IFT (σ_0 , mN/m)	Oil-Alkali IFT (σ , mN/m)	Surface Pressure (π , mN/m)	V_w/V_o
Distilled Water	27.3	-	-	-
1.25	27.3	3.7	23.6	160
2.50	27.3	1.5	25.8	170
12.50	27.3	0.05	27.25	150
25.0	27.3	0.06	27.24	150
125.0	27.3	0.17	27.13	150
250.0	27.3	0.27	27.03	150
375.0	27.3	0.30	27.0	150
500.0	27.3	0.40	26.9	150

Table A2 EQUILIBRIUM IFT DATA FOR NaOH / COURT CRUDE AT 45°C

NaOH Conc (mM)	Oil-Water IFT (σ_0 , mN/m)	Oil-Alkali IFT (σ , mN/m)	Surface Pressure (π , mN/m)	V_w/V_o
Distilled Water	24.4	-	-	-
1.25	24.4	8.6	15.45	83
2.50	24.4	5.47	18.57	83
25.0	24.4	0.17	23.87	150
125.0	24.4	0.15	23.89	150
250.0	24.4	0.18	23.86	150
375.0	24.4	0.19	23.85	150
500.0	24.4	0.24	23.80	150

Table A3 EQUILIBRIUM IFT DATA FOR NaOH / COURT CRUDE AT 75°C

NaOH Conc (mM)	Oil-Water IFT (σ_0 , mN/m)	Oil-Alkali IFT (σ , mN/m)	Surface Pressure (π , mN/m)	V_w/V_o
Distilled Water	24.20	-	-	-
1.25	24.20	13.84	10.36	71
2.50	24.20	7.20	17.0	77
125.0	24.20	0.90	23.30	150
250.0	24.20	0.81	23.39	150
375.0	24.20	1.21	22.99	150
500.0	24.20	0.84	23.36	150

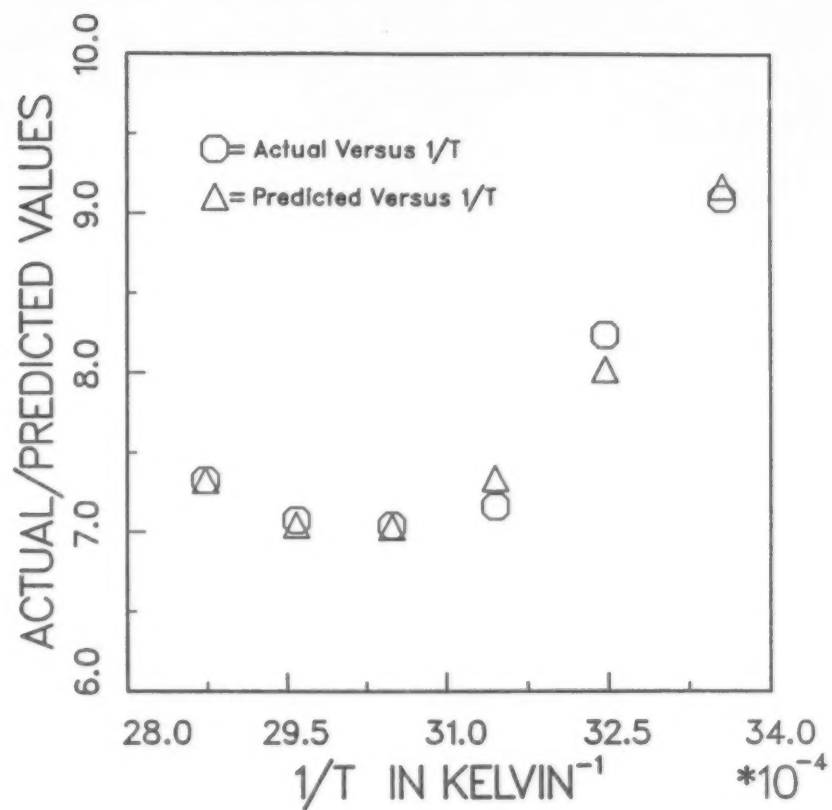


Fig. A1 : Variation of Actual and Predicted K_{HA}^D with $1/T$

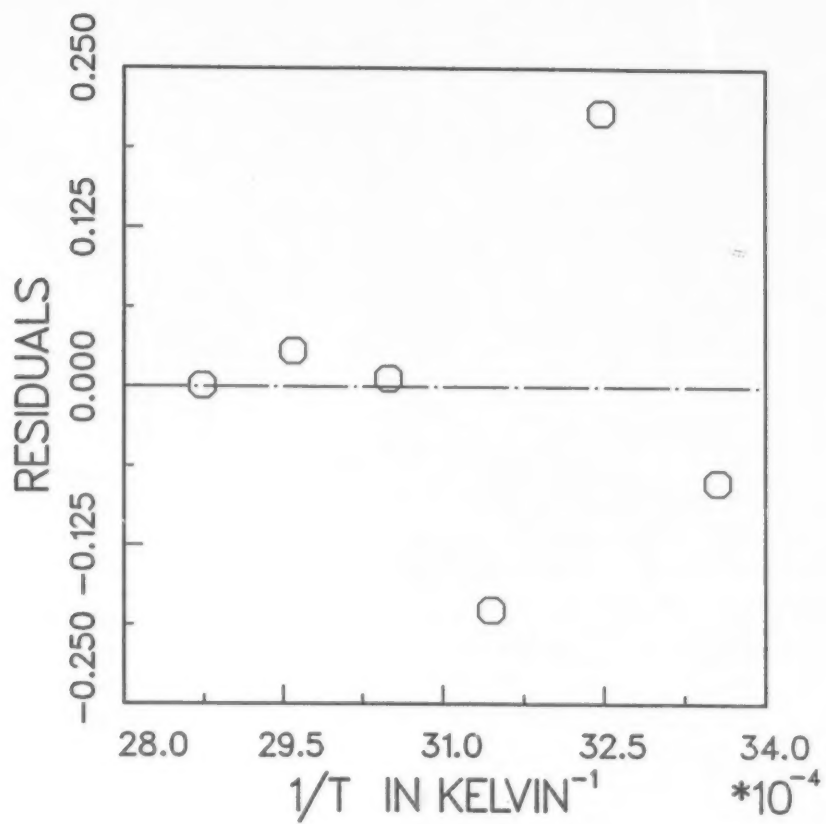


Fig. A2 : Residuals Versus $1/T$